ANALYTICA CHIMICA ACTA

International monthly dealing with every branch of analytical chemistry
Revue mensuelle internationale consacrée à tous les domaines de la chimie analytique
Internationale Monatsschrift für alle Gebiete der analytischen Chemie

Organe Officiel de la Section de Chimie Analytique de l'Union Internationale
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ELECTROPHORESIS AND
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Reviews

VOLUME I

Edited by
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$6^1/_2 \times 9^1/_2$″ *xii + 276 pages* *114 tables* *64 illus.* *1959*

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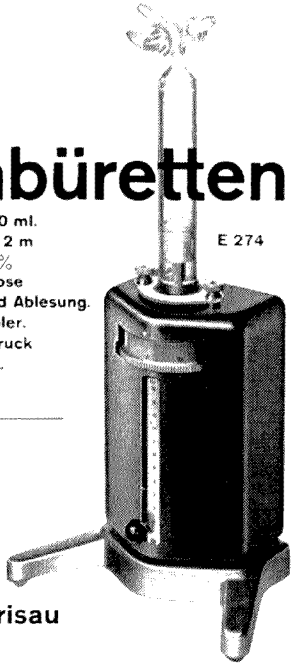

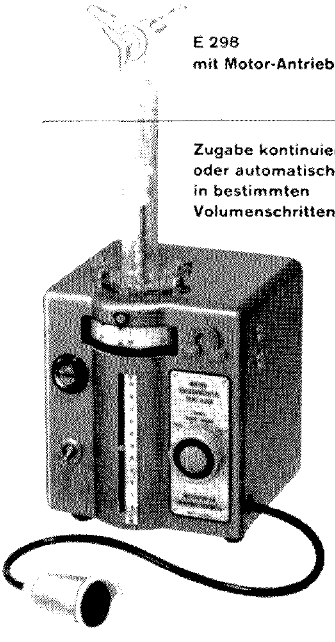

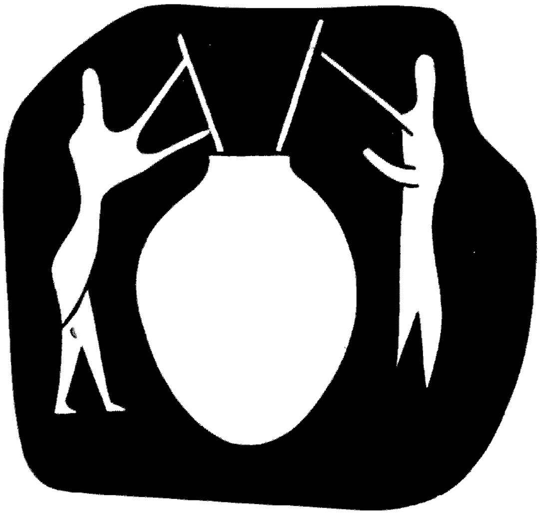

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A SYSTEMATIC SCHEME OF QUALITATIVE ANALYSIS FOR ANIONS. III

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In the present scheme[1] for the systematic analysis of anions, two new reagents have been introduced for the separation of anions into groups, namely, zinc nitrate or acetate and cadmium nitrate. The first precipitates a large number of anions and basic radicals which are separated into sub-groups by the use of other reagents. A systematic investigation was undertaken to determine the completeness of the precipitation of the anions and basic radicals by the group reagents. In those cases in which the anion is not completely precipitated but divides itself between the precipitate and the filtrate, the investigation roughly showed the distribution of the anions under these conditions.

METHOD

The method adopted in investigating the completeness of precipitation in the case of anions and basic radicals is described below.

A measured volume of a standard solution of the anion was treated with the group reagent, the precipitate was filtered off, dissolved in acid and the amount of its contained anion was estimated by the same method which was adopted in standardizing the solution. In cases where the solution of the anion was treated with sodium sulphide reagent, any acid present in the solution was neutralized with NaOH solution. In the case of basic radicals, the salt containing the basic radical was boiled with 10% sodium carbonate solution and the mixture filtered. One measured portion of the sodium carbonate filtrate was treated directly for the estimation of the basic radical. Another measured portion was first treated with a slight excess of zinc acetate solution, the precipitate filtered off and the basic radical it contained was estimated by the same method.

The results of this investigation are shown in Table I.

It can be seen from this table that arsenate, tellurate, tellurite, tungstate, selenite and phosphite are quantitatively precipitated by zinc acetate and selenate by cadmium nitrate. Therefore, these two reagents can be utilized for the gravimetric estimation of these anions. Detailed methods for their gravimetric estimations are being developed and may provide convenient and accurate methods for the estimation of many elements in the form of anions. Some of the anions precipitated completely by the group reagents in the scheme of qualitative analysis of anions, have not been included in this investigation; their methods of estimation using these reagents are already well-known.

TABLE I

Salt solution employed	*Standardized and estimated as*	*% error*
	Precipitation of anions by zinc acetate	
Potassium tellurate	TeS_3 [2]	±0.2 to 0.3
Potassium tellurite	TeS_2 [3]	±0.2 to 0.3
Potassium antimonate	Sb_2S_5 [4]	−0.1
Potassium antimonite	Sb_2S_3 [5]	±0.2
Potassium selenite	SeS_2 [3]	−0.4
Potassium periodate	Volumetrically	−0.8
Sodium arsenate	As_2S_5 [3]	±0.2
Sodium tungstate	WO_3	±0.3 to 0.4
Sodium phosphite	$(NH_4)_3PO_4 \cdot 12MoO_3$	±0.2
Sodium stannate	SnO_2	±0.3
		Percentage which passes into the filtrate
Sodium molybdate	$MoS_3 \cdot 2H_2O$ [6]	60.0
Potassium chromate	Volumetrically	80.0
Potassium arsenite	Volumetrically	10.0
	Precipitation of anions by cadmium nitrate	
Potassium selenate	Se_2S_5 [2]	±0.2
		Percentage which passes into the filtrate
Potassium iodate	Volumetrically	50.0
Potassium chromate	Volumetrically	80.0
	Precipitation of basic radicals in the sodium carbonate filtrate by zinc acetate	
Aluminium	Al_2O_3	+0.2 to 0.3
Beryllium	BeO	−2.0
Zirconium	ZrP_2O_7	+0.3
Thorium	$Th(IO_3)_4$	±0.3
Uranium	U_3O_8	−0.3
Copper	Volumetrically	−0.8
Cobalt (in presence of NH_4 salts)	Co_3O_4	−1.5
Nickel (in presence of NH_4 salts)	$Ni(C_4H_7O_2N_2)_2$	−1.6

ACKNOWLEDGEMENT

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SUMMARY

The completeness of precipitation of anions and basic radicals by the two group reagents, zinc acetate and cadmium nitrate, has been investigated. It has been shown that the two reagents precipitate many of the anions quantitatively and can thus be used for their gravimetric estimation.

RÉSUMÉ

Deux réactifs, l'acétate de zinc et le nitrate de cadmium, sont proposés pour la précipitation quantitative de nombreux anions, pouvant permettre un dosage gravimétrique.

ZUSAMMENFASSUNG

Die quantitative Fällung zahlreicher Anionen mit den Gruppen-Fällungsmittel Zinkacetat und Cadmiumnitrat wurde untersucht.

References p. 3

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A SYSTEMATIC STUDY OF INSOLUBLE SUBSTANCES. III

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In a series of papers[1-3] originating from this laboratory, many substances have been discussed which become resistant towards the solvent action of concentrated acids on heating to a high temperature. None of the tungstates, tellurates and vanadates have so far been included in the list of insoluble substances, but investigations carried out in this laboratory have shown that the metal salts of these acids, when heated to 800° for 2 h in a muffle furnace, are hardly soluble in acids.

Tungstates

The general method followed in the preparation of the tungstates consisted of adding an aqueous solution containing the chloride or sulphate of the metal to a hot dilute aqueous solution of normal sodium tungstate, Na_2WO_4. The precipitated tungstates were filtered, washed with water and heated at 800° in a muffle furnace for 2 h. Before the heated tungstates were subjected to the standard acid treatment, they were treated with dilute hydrochloric acid and sodium carbonate solution, successively, to dissolve the oxide of the metal and tungstic acid. The portion of the heated tungstate which dissolves in the standard acid treatment yields a precipitate of tungstic acid. This must be dissolved by washing firstly with a dilute solution of sodium carbonate and then with water containing a small amount of hydrochloric acid before weighing the remaining undissolved portion. Copper tungstate melts at high temperatures and thus was heated on the blow-pipe flame.

The insoluble tungstates were also analysed to determine their percentage composition. Weighed amounts of the heated tungstates were fused with caustic soda (adding potassium nitrate in the case of chromium salt) and the two metals were estimated by the well-known methods. The composition of the heated tungstates was found to be the same as that of the normal tungstates (anhydrous) reported in the literature[4] except in the case of the tungstates of chromium and zirconium. This is evident in the accompanying table.

In regard to the tungstates of Ca, Sr, Ba, Cd, Mn, Al and U, no appreciable change

TABLE I

Name of compound	*Percentage left undissolved in*				*0.01 g of the substance in 1 standard acid treatment*	*Formula given in literature*	*Formula found experimentally*
	2-h ignition at 800°		*9-h additional ignition at 800°*				
	1 standard acid treatment	*5 standard acid treatments*	*1 standard acid treatment*	*5 standard acid treatments*			
Tungstates							
1. Nickel tungstate	98.5	95.2	99.2	96.0	Does not dissolve completely	$NiWO_4$	$NiWO_4$
2. Cobalt tungstate	78.5	56.3	78.5	61.0		$CoWO_4$	$CoWO_4$
3. Chromium tungstate	88.2	76.0	88.2	78.0		$Cr_2O_3 \cdot 2\ WO_3$	$Cr_2O_3 \cdot 1.5\ WO_3$
4. Zirconium tungstate	90.0	88.8	94.2	90.3		—	$2\ ZrO_2 \cdot WO_3$
(5. Zinc tungstate	49.0	29.4	56.5	33.0		$ZnWO_4$	$ZnWO_4$)
(6. Copper tungstate	40.5	12.0	—	—		$CuWO_4$	$CuWO_4$)
Tellurates							
1. Chromium tellurate	99.5	99.0	—	—			
2. Zirconium tellurate	90.0	88.8	92.0	91.5			
Vanadates							
1. Chromium vanadate	89.5	88.6	—	—			
2. Zirconium vanadate	74.2	71.3	74.2	71.3			

in solubility was found on heating. The tungstates of zinc and copper also dissolved, to a great extent in the standard acid treatment.

Tellurates and vanadates

The behaviour of the tellurates and vanadates of most of the metals was investigated. Though the salts of these acids which dissolve with difficulty are precipitated on mixing solutions of potassium tellurate or ammonium vanadate with the aqueous solutions of these metallic salts, they are not rendered insoluble in acids on heating at a high temperature except in the case of the tellurates and vanadates of chromium and zirconium as shown in Table I. It should be noted that zirconium tellurate is not decomposed by alkaline fusion and has to be fused with potassium acid sulphate as in the case of the oxides of cerium, thorium and rhodium.

To determine to what degree the insoluble compounds would be affected in preparing the sodium carbonate filtrate for the detection of the anions, the heated compounds were boiled with about 10% sodium carbonate solution for 10 min. All the insoluble tungstates, tellurates and vanadates are decomposed slightly, enough to yield a positive result for the anion in the filtrate when testing. The chromites and aluminates reported in an earlier paper[3], and nickel tungstate are not at all affected by this treatment.

Note

The molybdates and selenates of most of the metals were prepared and heated at 900° for 2 h in a muffle furnace but none were rendered insoluble in acids.

SUMMARY

The tungstates of Ni, Co, Cr, Zr, Zn and Cu and the tellurates and vanadates of Cr and Zr, when heated at 800° were found to become sufficiently resistant to the standard acid treatement to be considered insoluble. The tungstates, tellurates and vanadates of other metals were not affected by heating.

RÉSUMÉ

Les tungstates de Ni, Co, Cr, Zr, Zn et Cu, ainsi que les tellurates et vanadates de Cr et Zr, chauffés à 800° deviennent suffisamment résistants à l'attaque par les acides pour être considérés comme insolubles. Par contre, le chauffage est sans influence sur les tungstates, tellurates et vanadates des autres métaux.

ZUSAMMENFASSUNG

Es wird nachgewiesen, dass die Wolframate von Ni, Co, Cr, Zr, Zn und Cu sowie die Tellurate und Vanadate von Cr und Zr durch Erhitzen auf 800° genügend säurebeständig werden, so dass sie als „unlöslich" betrachtet werden können. Die Löslichkeit der Wolframate, Tellurate und Vanadate anderer Metalle wird durch die Hitzebehandlung nicht beeinflusst.

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A STUDY OF THE PURITY AND UNIFORMITY OF COMPOSITION OF FERROUS AMMONIUM SULFATE HEXAHYDRATE AS A SOLID STANDARD REDUCTANT

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The use of ferrous ammonium sulfate hexahydrate (Mohr's salt) as a solid standard reductant has been discouraged because it is not amenable to a high degree of purification by recrystallization[1]. However, when the need arose for a method to assay ultrapure chromium to better than 0.1% on a routine basis, its high equivalent weight and simplicity of reaction with oxidizing solutions made its use seem highly attractive. The advantages of Mohr's salt over arsenious trioxide, an alternate choice of solid reductant which can be obtained in primary standard quality, include the the avoidance of the need for catalysis and the ease of its solubility in acidic solutions. Therefore, the following study of the purity and uniformity of composition of a commercially available analytical reagent was undertaken to determine its suitability for the proposed assay method for chromium metal[2]. It was anticipated that present-day manufacturing processes had sufficiently improved the quality of the available analytical reagent to permit its use as a "secondary" standard material.

As a basis for the following work, primary standard potassium dichromate was used as the fundamental reference of purity. To avoid volumetric errors, weighed quantities of solid reagent-grade ferrous ammonium sulfate hexahydrate were added in slight excess to solutions of known weights of the potassium dichromate. An amperometric titration, adapted from the work of PARK AND LYKKEN[3], was then used to measure the excess ferrous ion.

EXPERIMENTAL

Apparatus and reagents

The amperometric titration was performed in a 600-ml beaker accommodating a rotating platinum microelectrode, and the salt bridge connection from a saturated calomel reference electrode. The salt bridge was conveniently made from Tygon tubing filled with saturated potassium chloride and plugged by means of a short length of porous Vycor which may be obtained from the Corning Glass Works (Glass 7930)[4]. The microelectrode was rotated using a Sargent Synchronous Rotator, S-76485. Voltage was applied and the diffusion currents measured with a Sargent Ampot, S-29710. Stirring was accomplished magnetically using a Teflon-covered stirring bar, and titrations were made from a 10-ml microburet.

The ferrous ammonium sulfate hexahydrate studied was the Analytical Reagent grade supplied by the Mallinckrodt Chemical Works. Both catalog items, 5064 and 5068 ("low manganese" content), were used. Primary Standard, Analytical Reagent, potassium dichromate was also obtained from Mallinckrodt. A 0.0200*N* solution of potassium dichromate was prepared directly from the primary standard material. All other solutions were prepared from analytical grade reagents.

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Procedure

Approximately 1.4 g of primary standard potassium dichromate was accurately weighed, and dissolved in about 300 ml of distilled water. The solution was then acidified with 30 ml 1:1 sulfuric acid and 6 ml of 1:1 nitric acid and cooled to room temperature. A calculated amount of ferrous ammonium sulfate hexahydrate was weighed to the nearest 0.1 mg to provide an excess of about 0.1 milliequivalent greater than the equivalents of dichromate. As a first approximation, the purity of the ferrous ammonium sulfate was assumed to be 100%. The weighed reagent was added directly to the dichromate solution which was then stirred magnetically for approximately 3 min to completely dissolve the salt. After immersing the platinum electrode and connecting salt bridge in the solution ±1.0 V was applied to the rotating platinum electrode. An anodic current of approximately 30 μA indicated the presence of excess ferrous ion. The initial current was recorded, and the titration was performed in the usual manner using 0.0200*N* potassium dichromate in 2-ml increments. The current decreased linearly to zero at the end-point. From the total number of milliequivalents of potassium dichromate consumed, and the weight of ferrous ammonium sulfate hexahydrate taken, the purity of the latter was calculated.

RESULTS

In order to evaluate the homogeneity of ferrous ammonium sulfate hexahydrate within a bottle, one pound was carefully quartered without prior mixing, and three assay analyses performed on each quarter. The results, shown in Table I, indicated a remarkable constancy of composition as well as high purity. The standard deviation, representing the total variability of the measurements as well as any variability in the composition of the salt, indicated a precision of about two parts per ten thousand. The reliability of this estimate of precision, calculated by its upper 99% confidence limit, indicated a probability of only one in a hundred that the estimated precision was actually greater than four parts in ten thousand. One may conclude that the material in this bottle was essentially homogeneous and that the method was capable of high precision.

TABLE I

ASSAY (IN %) AND HOMOGENEITY OF A ONE-POUND BOTTLE OF FERROUS AMMONIUM SULFATE HEXAHYDRATE[a] AGAINST PRIMARY STANDARD POTASSIUM DICHROMATE[b]

Quarter[c]	*1*	*2*	*3*	*4*
	99.92	99.89	99.87	99.82
	99.84	99.83	99.84	99.87
	99.87	99.89	99.85	99.86
Average	99.88	99.87	99.85	99.85
Grand average				99.862
99% Confidence limits of grand average				99.841 – 99.883
Standard deviation of an individual measurement				±0.023 ($n = 12$)
99% Upper confidence limit of the standard deviation				0.044

[a] Mallinckrodt Catalog #5064.
[b] Mallinckrodt Catalog #6772.
[c] Contents of bottle quartered, without mixing, prior to analysis.

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TABLE II

COMPARISON OF ASSAYS (IN %) AND HOMOGENEITIES OF THREE ONE-POUND BOTTLES OF FERROUS AMMONIUM SULFATE HEXAHYDRATE AGAINST PRIMARY STANDARD POTASSIUM DICHROMATE

Bottle	1[a]	2[b]	3[c]
Average	99.862	99.852	99.871
99% Confidence limits of average	99.841–99.883	99.825–99.879	99.849–99.893
Standard deviation of an individual measurement[d]	±0.023	±0.030	±0.024
99% Upper confidence limit of the standard deviation	0.044	0.057	0.046

[a] Mallinckrodt Catalog #5064; data reported in Table I.
[b] Mallinckrodt Catalog #5064
[c] Mallinckrodt Catalog #5068.
[d] $n = 12$ for each estimate.

Table II shows the results obtained with two additional one-pound bottles of ferrous ammonium sulfate hexahydrate where one of these was the "low manganese" grade of analytical reagent. The same experimental design previously described was used. Included in Table II are the results of the analyses on the first bottle tested (Table I), and a comparison of the three standard deviations indicates the same high degree of homogeneity in each bottle. In addition, the assays of these three individual one-pound quantities were notably the same despite the fact that at least one of them ("low manganese" grade) was purchased as a separate catalog item (5068).

Ten months after the data shown in Table II had been obtained, the hydrate in bottle 2 was re-assayed to detect any change in its reducing power. No special precautions had been taken to safeguard its quality except to keep it stored in the original bottle with its plastic screw cap. Occasional use had been made of this material over this period. Table III summarizes the re-assay data which shows a slight but significant decrease of about 0.05% in its effectiveness as a reductant.

TABLE III

RE-ASSAY OF FERROUS AMMONIUM SULFATE HEXAHYDRATE (Bottle 2, Table II) AFTER A PERIOD OF TEN MONTHS. STUDY OF THE EFFECT OF PHOSPHORIC ACID ON THE AMPEROMETRIC TITRATION

	Phosphoric acid present	*Phosphoric acid absent*
	99.81	99.80
	99.80	99.79
	99.81	99.80
	99.81	99.81
	99.82	99.79
	99.80	99.82
Average	99.808	99.802
Grand average	99.805	
99% Confidence limits of grand average		99.795–99.815
Standard deviation of an individual measurement		±0.011 ($n = 12$)
99% Upper confidence limit of the standard deviation		0.021

In conjunction with this assay, the effect of phosphoric acid, which shifts the oxidation of the ferric-ferrous system in favor of more complete reaction with dichromate, was also studied. As indicated in the table where 6 results were obtained in the presence of phosphoric acid (5 ml of 85% phosphoric acid added to solution prior to titration according to above procedure) and 6 without it, essentially identical assays were obtained in both cases indicating that the use of phosphoric acid is unnecessary with an amperometric end-point.

DISCUSSION AND CONCLUSIONS

Although the work reported is necessarily a very limited sampling of the commercially available reagent, it indicates that the Mallinckrodt product, in particular, is suitable with respect to both its high purity and uniformity of composition as a secondary-standard solid reductant. Without extensive evaluation of homogeneity, other one-pound quantities, which were obtained periodically, have also been found to possess essentially the same high purity. In several cases, the appearance of the reagent with respect to its crystallinity would make us suspect that differences in reducing power would be found because of varying water content. However, subsequent evaluation of such lots has not revealed a significant difference in their assay.

SUMMARY

A study of the purity and uniformity of composition of commercially available ferrous ammonium sulfate hexahydrate has been undertaken to determine its suitability as a solid standard reductant. Weighed quantities of reagent-grade Mohr's salt were added in slight excess to solutions of known weights of primary standard potassium dichromate. An amperometric titration was then used to measure the excess ferrous ion. Results found indicate that present-day manufacturing processes have sufficiently improved the quality of the available analytical reagent to permit its use as a secondary-standard solid reductant.

RÉSUMÉ

On a examiné le sulfate double de fer(II) et d'ammonium (sel de Mohr) en vue de son utilisation comme étalon en chimie analytique. Des quantités déterminées de ce réactif ont été ajoutées en léger excès à des solutions de dichromate de potassium titrées. On a mesuré ensuite l'excès de fer(II) par ampérométrie.

ZUSAMMENFASSUNG

Das Eisen-(2)-ammoniumsulfat (Mohr'sches Salz) wurde auf seine Eignung als Standard-Reduktionsmittel für die analytische Chemie untersucht. Gewogene Mengen des Eisen-(2)-Salzes wurden in geringen Überschuss zu einer Lösung mit bekanntem Kaliumbichromatgehalt gegeben und der Überschuss an Eisen-(2)-Salz amperometrisch ermittelt.

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THE CONDUCTOMETRIC TITRATION OF CARBOXYLIC AND PHENOLIC ACIDS IN NON-AQUEOUS SOLUTIONS

II. STUDY OF THE TITRATION OF DIBASIC ACIDS

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INTRODUCTION

The conductometric titration of dibasic acids in non-aqueous solvents using tetramethylammonium hydroxide as a base yields conductance curves of various shapes, depending on the acid as well as on the solvent employed[1]. In some solvents the strongest dibasic acids, *i.e.* those in which the ratio of the two ionization constants in water is 100 or more (oxalic, phthalic acid etc.), give N-shaped titration curves, the conductance of the solution showing a minimum at the second equivalence point, not caused by formation of a precipitate. (The occurrence of an N-shaped curve as a result of precipitate formation after the first equivalence point will not be discussed.) In other solvents no minimum is observed with these acids and the titration curve has the shape of a chair. Weaker acids such as isophthalic acid generally show the latter behaviour in all solvents.

In the present investigation the factors determining the shape of the titration curves of dibasic acids in non-aqueous media were studied more thoroughly. Thus titrations with other bases, some of them giving salts which are soluble in most solvents, were performed. The base used by preference was tetra-*n*-butylammonium hydroxide; other bases, less frequently used, were diethylamine and piperidine, and lithium and potassium methoxide.

The factors under consideration are: (1) The distance between the acid groups; (2) The properties of the solvent, in particular: a. the solvating power (presence of groups forming hydrogen bonds, such as —OH); b. the mean dielectric constant; (3) The size of the base cation; (4) The temperature.

From the results of the study of these factors the conditions can be found for producing the most suitable titration curves and hence for obtaining maximum accuracy in the determination of the equivalence points.

EXPERIMENTAL

Solvents and titrants

The purification of the solvents and the preparation of the quaternary ammonium bases were described in the previous paper[1]; tetrabutylammonium hydroxide was made in the same way as the tetramethylammonium hydroxide solution. The strength of the tetrabutylammonium hydroxide solutions used varied between 0.1 *N* and 0.3 *N*, that of the tetramethylammonium hydroxide was 0.1 *N*. The strongest solutions consisted of the hydroxide dissolved in equal parts by volume of methanol and benzene; with the decinormal solutions the methanol–benzene ratio was either 1 : 3 or 1 : 4 (v/v).

For the diethylamine and piperidine titrants we made solutions of the freshly distilled compounds in methanol. The strength of both bases was 0.2 *N*.

The two methoxides were prepared by dissolving the required amount of metal in methanol. The strength of these bases was 0.1 *N*.

Apparatus

In most of the titrations the resistances were measured with the equipment described previously[1]; the relative accuracy was better than 1%. For the titrations with piperidine and diethylamine as titrants, however, the normal apparatus was not sufficiently sensitive, so that at higher resistances the error rapidly increased to 1–5%. Therefore a new bridge was built, which was fed by an audio-frequency oscillator and used a cathode-ray oscilloscope as the zero-point indicator. With this bridge all titrations could be carried out satisfactorily.

For the titrations at higher temperatures a jacketed cylindrical glass vessel closed by a cork plug was used. This plug was provided with holes for the dip-electrode assembly (cell constant ∿0.8 cm^{-1}), a thermometer and the burette tip. Water from a thermostat circulating through the cell jacket permitted temperature control to approx. 0.05° at the three temperatures used (25°, 50° and 70°). During titration the solution was stirred with a magnetic stirrer.

Titration procedure

For every titration the acid was brought into the titration vessel, either by weighing the pure compound or by pipetting a standard solution in such a quantity, that about 1 ml of base was required per acid group. Then the volume was made up to 40–60 ml and the solution stirred until it had attained the temperature of the thermostatted vessel. Small portions of base were added (approx. 0.10 ml from a semi-micro burette) and the readings were taken when they became constant. This was normally the case within half a minute.

DISCUSSION OF RESULTS

a. Influence of the distance between the acid groups

The experimental results indicate that in general the dibasic acids, so far as the conductometric titration in non-aqueous media is concerned, may be divided into two groups: those that are able to give N-shaped titration curves, and those that will, under any conditions, only give chair-shaped curves.

The first group comprises the acids for which the K_1/K_2 ratio in water is 100 or more (sulphuric, oxalic, malonic, maleic and phthalic acid), the second group consists of those for which this ratio is lower than 100, in general 10–40 (sebacic acid: 10, adipic acid: 35[2]. (Figs. 1 and 2) (K_1 and K_2 are the first and the second ionization constant, respectively.)

There are a few exceptions to this rule, however: succinic, glutaric, malic and tartaric acid, for instance, which have a K_1/K_2 ratio in water lower than 100, nevertheless give N-shaped titration curves under the same conditions as malonic acid. Hence, as far as titration in non-aqueous media is concerned these acids belong to the first group. The explanation of this phenomenon will be given in a later paper.

The behaviour of adipic and fumaric acid (Figs. 1 and 2) is intermediate between these two groups: in most cases a chair-shaped curve is obtained, but under special conditions (see d.) an N shape is also possible.

From the experiments it can be seen that acids, in which the distance between the carboxylic groups is at least 8 Å[3], give chair-shaped curves only. In the series of the α,ω-dicarboxylic acids this applies to adipic acid and the higher homologues. For isophthalic and terephthalic acid this statement does not hold: these acids give chair-shaped curves although the distance is only 5–6 Å, but here the rigid structure plays an important role. For further details the reader is referred to a forthcoming paper.

b. Influence of solvent

The most important properties of the solvent influencing the titration are its dielectric constant ε and its solvating power.

The first of these will determine the electrostatic forces acting between the ions and hence the degree of ionization of the salts of a dibasic acid[1]. The ionization of the acid salts is, however, less influenced by changes in the dielectric constant than that of the neutral salts. The influence of ε is illustrated in Fig. 3 by the shape of the titration curve of malonic acid in dimethylformamide(DMF)-benzene mixtures, which shows that optimum results with respect to the accuracy in the determination of the intersections are obtained at values of ε below 20, *i.e.* for a DMF/benzene volume ratio below 1 : 1 (the approximate values of ε were calculated on the assumption that $\varepsilon_{\text{solvent}} = x_1\varepsilon_1 + x_2\varepsilon_2$, in which x_n = mole fraction of compound n).

These titrations are complicated, however, by the strongly decreasing conductance of the solutions, hence it will be practically impossible to use DMF/benzene ratios below 1 : 4. For the same reason the use of pyridine-benzene mixtures was unsuccessful.

Similar results are obtained when titrating in alcohol-benzene mixtures with lithium or potassium methoxide (Fig. 4) or with tetramethylammonium hydroxide. In these systems the amount of benzene also determines the conductance of the solutions to a great extent.

The second property of the solvent, its solvating power, is more important than the first. In pure methanol, for instance, it is impossible to obtain N-shaped titration

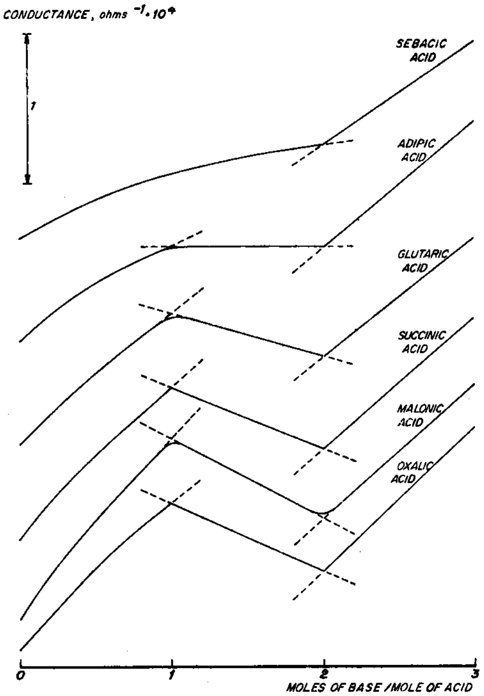

Fig. 1. Titration of α, ω-dicarboxylic acids in pyridine with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

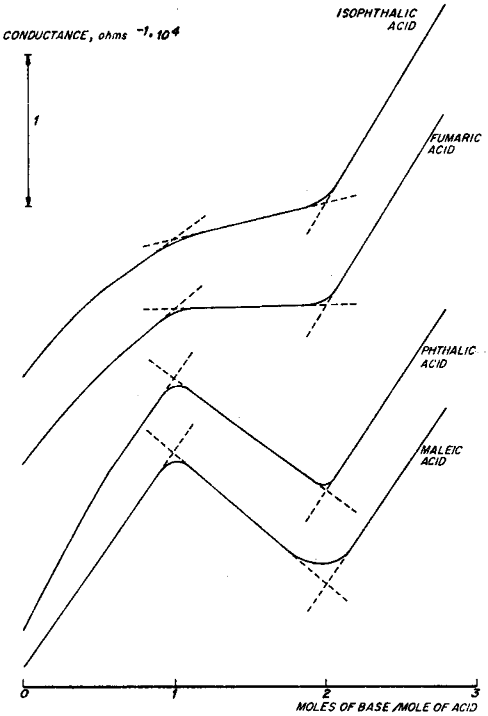

Fig. 2. Titration of some dicarboxylic acids in pyridine with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

curves when using quaternary ammonium bases, whereas in pure propanol-2, as a consequence of its lower solvating power, N-shaped curves are often found when tetramethylammonium hydroxide is used. As a matter of fact, the decrease in dielectric constant, if one goes from methanol ($\varepsilon_{25} = 32.6$) to propanol-2 ($\varepsilon_{25} = 18.3$), partly accounts for the change in behaviour. The solvating properties of the solvent are predominant, however, as is clearly proved by the titration of phthalic acid with tetrabutylammonium hydroxide in methanol–benzene (1 : 3 v/v); this solvent has approximately the same dielectric constant ($\varepsilon \approx 13$) as pyridine, but as a consequence of the methanol present no N-shaped curve could be obtained in it. In non-solvating media such as pyridine and DMF, N-shaped curves may be obtained more often and hence these solvents are to be preferred for analytical purposes.

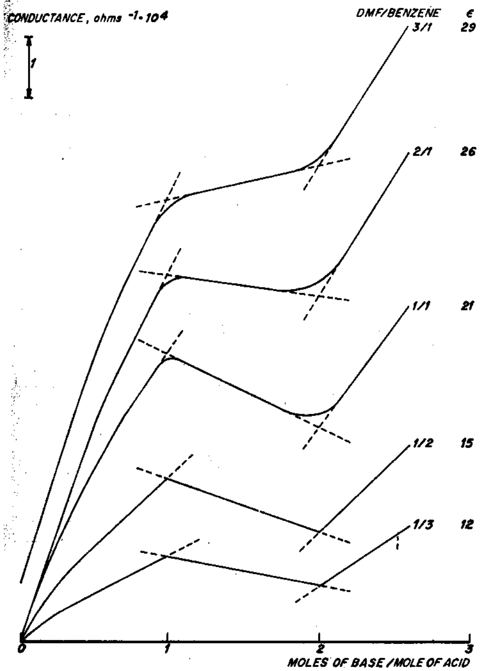

Fig. 3. Titration of malonic acid in DMF–benzene mixtures of different ratios (v/v) with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

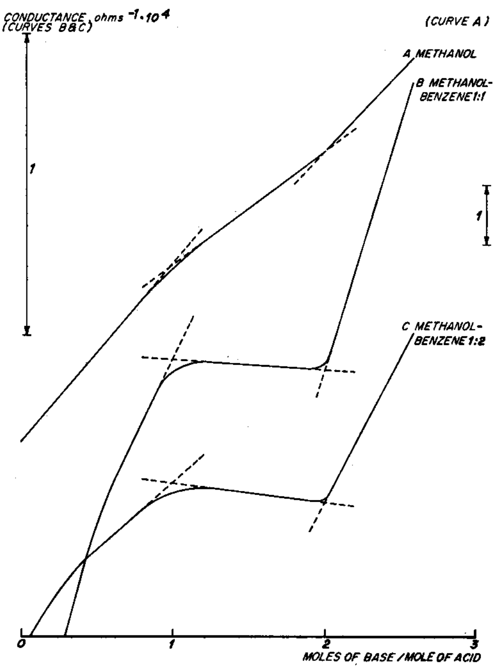

Fig. 4. Titration of succinic acid in methanol–benzene mixtures of different ratios (v/v) with potassium methoxide (curves have been drawn on different scales and have been shifted vertically for clarity).

c. *Influence of base cations*

It has often been observed that one base gives titration curves very different from those obtained with another. An example of this phenomenon is shown in Fig. 5, representing the titration of phthalic acid in methanol with tetramethyl- and tetrabutylammonium hydroxide and with piperidine. Similar results are obtained in alcohol–benzene mixtures with lithium or potassium methoxide (*cf.* Fig. 4 and ref. 4).

Titration of dibasic acids should, according to this evidence, preferably be carried out with bases derived from small cations (Li^+, K^+, Me_4N^+) or with amines. The applicability of such bases is, however, limited, as in most cases neutral salts of these bases and dibasic acids are insoluble in non-solvating media such as pyridine and DMF. The solubility of the lithium and potassium salts formed is low even in some solvating media such as propanol-2 and some methanol–benzene mixtures. It should further be mentioned that in most titrations carried out in alcoholic media the equivalence points cannot be determined accurately as a result of solvolysis. The changes in conductance in titrations with amines are in general too small for reliable determinations.

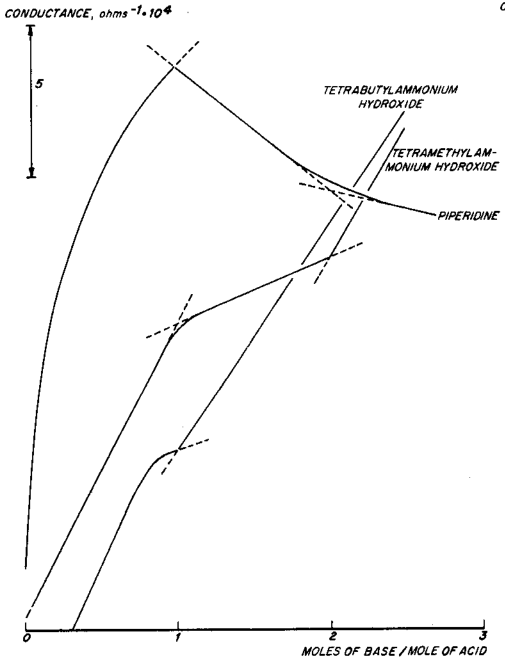

Fig. 5. Titration of phthalic acid in methanol with different bases (curves have been shifted vertically for clarity).

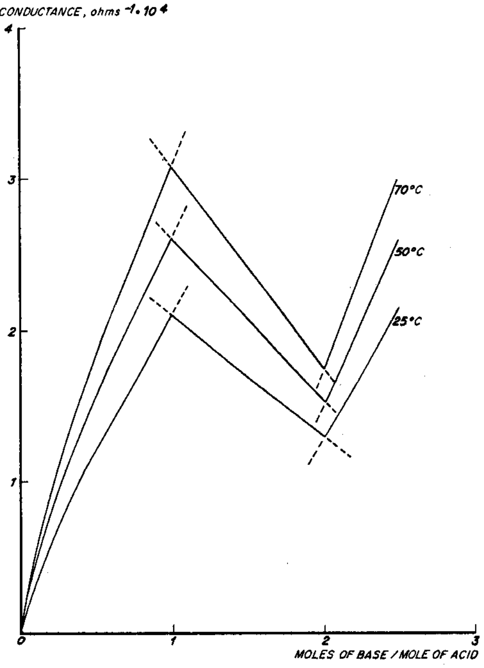

Fig. 6. Titration of succinic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

Summarizing, the base giving the best analytical results is tetrabutylammonium hydroxide, provided the titrations are carried out in non-solvating media of fairly low dielectric constant. Such titrations, especially in mixtures, will be dealt with in a future paper.

d. Influence of temperature

If the titrations are performed at higher temperatures the shapes of the curves are significantly changed for some acids, whereas for others there is hardly any temperature influence apart from an overall increase in conductance.

Figs. 6, 7 and 8 illustrate the temperature effect. Fig. 6 shows the titration curve of succinic acid in pyridine with tetrabutylammonium hydroxide at 25°, 50° and 70° (the other members of the first group of acids — *cf.* a. — give similar curves).

No pronounced change in shape takes place as the temperature is raised except that the N shape becomes just a little sharper.

Nor does the chair-shaped curve of isophthalic acid alter under these circumstances (Fig. 7). In the case of fumaric and adipic acid, however, a definite change was noted, the curve turning from chair-shaped at 25° to weakly N-shaped at 70° (Fig. 8). One observes similar effects in alcoholic media when titrating with other bases. *e.g.* in methanol–benzene (1 : 1 v/v) with lithium or potassium methoxide or in propanol-2 with tetramethylammonium hydroxide.

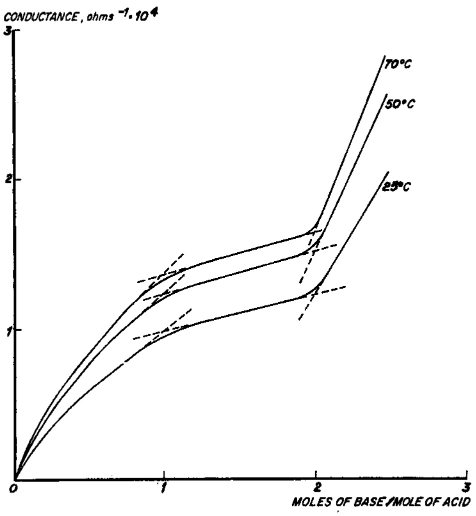

Fig. 7. Titration of isophthalic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

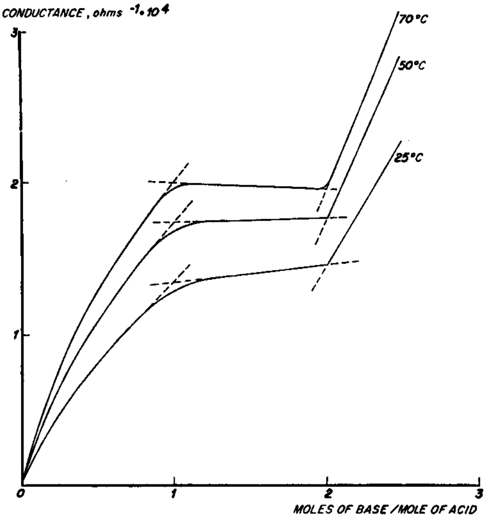

Fig. 8. Titration of adipic acid in pyridine with tetrabutylammonium hydroxide at different temperatures.

The change in the shape of the titration curves is not, as might be supposed, caused by the decrease in the dielectric constant of the solvent. The ε value of pyridine decreases from 12.3 at 25°[5] to about 10.8 at 70°. A mixture consisting of 5 vol. of pyridine and 1 vol. of benzene has the same ε value at 25°. Titration of adipic, fumaric and isophthalic acid in this solvent at room temperature showed that the decrease in ε at 25° does not affect the shape of the titration curves in the same way as does the rise in temperature by 45 degrees (Fig. 9).

The explanation of this temperature influence will be given in a forthcoming paper.

From the experiments it is seen that for analytical purposes (accurate determination of the equivalence points) it may be profitable to titrate at higher temperatures.

CONCLUSIONS

From the experiments described it can be concluded that for the conductometric titration of dibasic acids media of low solvating power and with a low dielectric constant are to be preferred. Of the titrants investigated tetrabutylammonium hydroxide gave the best results.

Titration at higher temperatures, up to 70°, in some cases increases the accuracy in the determination of the end-points.

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ACKNOWLEDGEMENT

The authors are much indebted to Miss A. Snip and the late Mr. P. J. Lafargue who skilfully carried out many of the experiments. They also wish to express their gratitude to Dr. Ir. P. N. Degens, Jr. for his stimulating interest in this investigation.

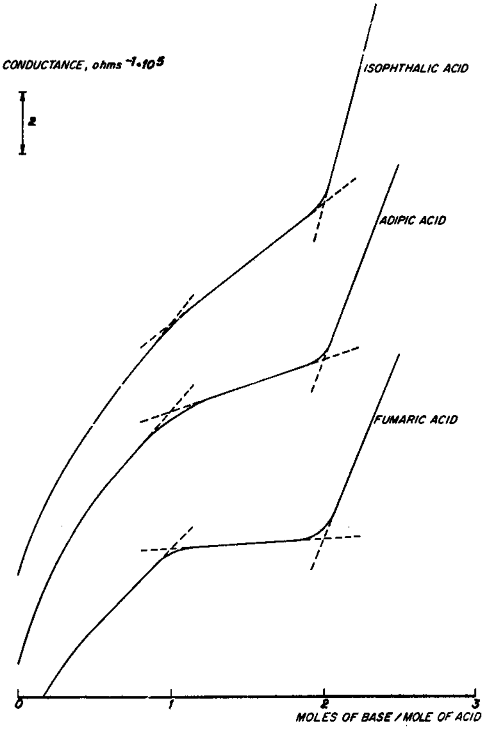

Fig. 9. Titration of adipic, fumaric and isophthalic acid in pyridine–benzene (5 : 1 v/v) with tetrabutylammonium hydroxide (curves have been shifted vertically for clarity).

SUMMARY

An experimental study has been made of the conductometric titration of dibasic acids in non-aqueous solvents.

The factors governing the shape of the titration curve and hence determining the accuracy of the analysis of these compounds are discussed, and the conditions are given under which optimum results are obtained.

RÉSUMÉ

Une étude expérimentale a été effectuée sur le titrage conductométrique des acides dibasiques en solvants non-aqueux.

ZUSAMMENFASSUNG

Es wird über ein konduktometrisches Titrationsverfahren zur Bestimmung zwei-basischer Säuren in nicht-wässrigem Lösungsmittel berichtet.

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VOLTAMMETRIC, POTENTIOMETRIC AND AMPEROMETRIC STUDIES WITH A ROTATED ALUMINUM WIRE ELECTRODE

I. VOLTAMMETRIC BEHAVIOR OF THE R.AL.E.

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The aluminum electrode is a highly polarizable electrode both anodically and cathodically, the passivity of the metal being attributed to a film of aluminum oxide covering the electrode surface. The electrode potentials measured by electrochemical techniques do not agree with the values calculated from thermodynamic data. Based on free energy data, LATIMER[1] calculated the standard electrode potential for the reaction: $Al = Al^{+3}$ (aq.) + 3e to be equal to —1.66 V *versus* the normal hydrogen electrode. However, potential measurements at a "pure" aluminum electrode give values which are much less negative than those corresponding to the above standard potential. Using an aluminum amalgam electrode, HEYROVSKY[2] calculated a value for the electrode potential of —1.337 V with reference to the normal hydrogen electrode.

The use of aluminum sheet (99.99% pure) as a pH-indicator electrode has been recommended by SCARANO[3] in potentiometric titrations of acids with bases. Reponse to pH, however, has not been reported. It is only stated that a large break in potential occurred at or near the equivalence point, but no potential data are reported in solution of a given pH.

After completion of our work, PLUMB[4] using electrodes which were made free of oxide by scraping the surface with alumina, reported values of potentials after different periods of time in oxygen-saturated solutions of various pH. He extrapolated the values to zero time (zero oxide thickness) and considered them to correspond to the potentials of the oxide-free electrode. The potentials thus obtained differed by more than 0.6 V from the values calculated on the basis of LATIMER's standard potential. PLUMB offers an interpretation for this discrepancy. It should be realized, however, that the anodic reaction at an aluminum electrode differs from the cathodic reaction and the potential therefore does not correspond to that of a reversible system.

According to our findings, in acid medium a pure aluminum electrode does not function as a pH electrode. In agreement with PLUMB it was found that the potentials in solutions containing excess of hydroxyl ions are fairly reproducible. As a matter of fact, the aluminum electrode does not function as a pH electrode but it does as a pOH electrode in the presence of an excess of hydroxyl ions. In acid media containing fluoride the depolarization potential is fairly reproducible and found to vary with pH and fluoride concentration. However, when exact information concerning the change in pH during a potentiometric titration is desired, the aluminum electrode, even in the presence of a trace of fluoride, cannot be recommended as a substitute for the host of readily available and more precise pH-indicator electrodes.

We have made an extensive study of the voltammetric properties of a rotated aluminum wire electrode in various supporting electrolytes. Of all ions tested only hydroxyl and fluoride ions were found to depolarize the electrode anodically at very high negative potentials. Use of this fact is made in a rapid amperometric method for the determination of fluoride in solution and in the amperometric titration of fluoride with a suitable cation, to be described in subsequent papers.

The main characteristic of the current-potential curves (voltammograms) in the absence of depolarizing hydroxyl and fluoride ions, is that the electrode remains highly polarized over a wide range of potentials both in the presence and absence of oxygen. This means that the electrode potential is ill-defined and hard to reproduce. In connection with the voltammetric studies potentials were measured in different media of varying pH and the results are described and discussed in the present paper.

EXPERIMENTAL

Materials

Pure aluminum wire. Aluminum rod, 1/16 inch diameter was prepared for us by the Aluminum Company of America and we like to express our sincere appreciation to this company for this courtesy. The reported analysis stated that the sample was composed of: Al, 99.99%; Cu, 0.001%; Si, 0.001%; Zn, 0.005%; others, 0.000%. Conductivity water and reagent chemicals were used in all experiments. In registering current-potential curves in the absence of oxygen an inert atmosphere was maintained by passing 99.99% pure nitrogen obtained from Linde Air Products Co.

Instrumentation.

Current-potential curves were recorded with a Leeds and Northrup Electrochemograph. For the measurements of current at a given potential both the polarograph and a manual apparatus were used. Potentiometric readings were taken with a Leeds and Northrup Student potentiometer. All experiments were carried out at 25°. The pH of all buffered and unbuffered solutions was measured with a Beckman glass electrode pH meter, after the equilibrium potential of the aluminum electrode had been measured. Determinations were carried out in a 100-ml cell equipped with an inlet tube for the introduction of nitrogen which was passed through the solution until it was oxygen-free and then over the solution during the recording of voltammograms. Connection to the saturated calomel electrode was made with a sodium nitrate salt bridge to prevent diffusion of chloride ions into the solution. Unless otherwise stated, the measurements were run from positive to negative potentials. Reported potentials refer to the S.C.E.

Construction of electrode

Considerable difficulty was encountered in constructing a satisfactory rotating aluminum electrode, hereafter designated as R.Al.E. The model depicted in Fig. 1 has been found suitable. It has been prepared in the following way: a straight piece of pure aluminum rod (10 cm long, 1.5 mm outside diameter) was attached by means of a screw joint to a short piece of stainless steel rod (2 cm long, 3 mm outside diameter). This assembly was introduced into two glass tubes, the upper part of which was 8 cm long and 0.6 cm wide, with a bore size of 0.5 cm, while the lower one was an equally wide tube, 9.4 cm in length but only 0.2 cm in bore size. The top tube contained only the stainless steel rod whereas the aluminum wire was contained in the narrow tube except that 0.6 cm protruded from the end. With the aid of a non-conducting film of adhesive cement the electrode was cemented to the bottom of the narrow tube leaving about 0.5 cm of aluminum exposed to the environment. This uncovered part of the wire served as electrode. The cement coating proved to be effective in insulating and very durable. A thin layer of apiezon W wax may also be used in place of the cement. To avoid any possibility of contact between mercury and the aluminum, a thick layer of apiezon W wax was placed and melted into the upper tube covering half of the stainless steel rod. The rest of the tube was filled with mercury to make electrical connection. The electrode was rotated at 600 r.p.m. by means of a Sargent synchronous motor.

Pretreatment of the R.Al.E.

The electrode was initally polished with emery paper, then it was kept in concentrated nitric acid for 30 min and thoroughly washed with distilled water before use. The same electrode was employed throughout all the experiments. Later a new electrode was constructed and its behavior was found to be closely similar to that of the first electrode. Great difficulties were experienced in reproducing current-potential curves. Their shapes and the zero current potentials were found to vary greatly with the pretreatment of the electrode, after a run had been made. The following types of treatment did not improve the reproducibility: cleaning with sand paper followed by anodic and cathodic polarization in acetate buffer pH = 3 at 1 V *versus* S.C.E. for 1 min pretreatment in concentrated nitric acid followed by the same polarization; cleaning in 0.1*M* sodium hydroxide in the absence or presence of 0.3*M* cyanide as recommended by SCARANO[8]; this treatment supposedly dissolves a film of oxide; cleaning in 0.05*M* sodium fluoride. Finally it appeared that the most reproducible results were obtained by keeping the electrode for about 20 min in a 0.02*M* solution of ethylenediaminetetraacetate in 0.2*M* acetic acid, pH 3, followed by anodic and cathodic polarization for 1 min at 1 V *versus* S.C.E. in this medium.

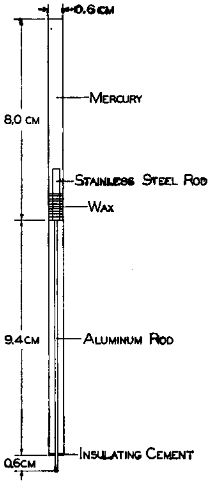

Fig. 1. The rotated aluminum electrode.

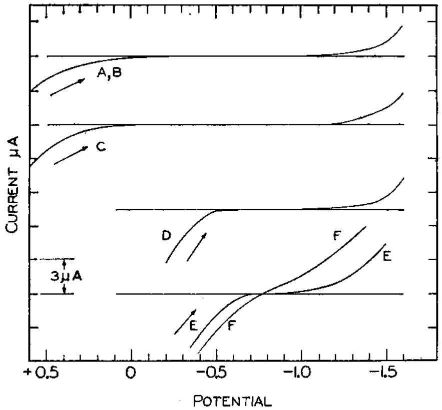

Fig. 2. Voltammograms measured from positive to negative potentials in oxygen-free solutions of: A, 0.2*M* HAc; B, 0.01*M* $NaNO_3$; C, 0.017*M* sodium benzoate; D, 0.01*M* $NaClO_4$; E, 0.01*M* $HClO_4$; F, 0.1*M* $HClO_4$.

Current-potential curves

The shapes of current-potential curves measured in various supporting electrolytes are shown in Figs. 2, 3 and 4. Each curve shown in Fig. 2 was recorded automatically from positive to negative potentials starting at +0.6 V *versus* S.C.E. with a scanning rate of 3.3 mV per second. Before each run the R.Al.E. was cleaned by the recommended procedure.

Voltammograms in Figs. 3 and 4 were run from positive to negative potentials and then in the reverse direction starting at —1.5 V. The electrode was then cleaned before placing in another electrolyte solution. The general shape of the curves in Fig. 3 is the same whether run from positive to negative or negative to positive potentials. In supporting electrolytes composed of an acetate buffer alone or with nitrate (Fig. 2), benzoate, phosphate (Fig. 3), sulfate or EDTA the electrode is strongly polarized from about +0.6 to —1.4 V, and the electrode potential (zero current–potential) is poorly defined and difficult to reproduce.

From Fig. 4 it is seen that perchlorate, chloride and bromide depolarize the electrode anodically. When the curves are run from positive to negative potentials, the anodic depolarization starts near —0.6 V, but at less negative potentials when run from negative to positive potentials. Under the latter conditions the lines representing the anodic currents are more drawn out. The values of the depolarization potentials also change with concentration of depolarizing anions. Voltammograms were also run in air-saturated solutions. In all instances the curves had the same appearance as in oxygen-free solutions, except that in the same electrolyte solution the potential was about 0.15 V less negative in the presence than in the absence of oxygen. Evidently, oxygen does not depolarize the electrode cathodically.

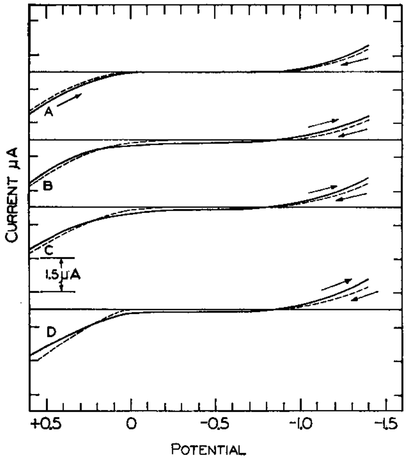

Fig. 3. Voltammograms in 0.2M HAc + 0.05M NaAc, pH = 4.0. A, no addition; B, 0.01M in Na_2SO_4; C, 0.01M in $NaNO_3$; D, 0.01M in $NaH_2PO_4 \cdot H_2O$. Dotted lines, potential changed from — to + values.

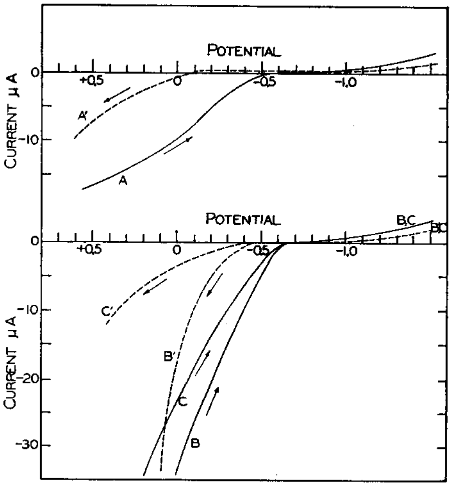

Fig. 4. Effect of chloride, bromide and perchlorate in acetate buffer (pH = 4.0). A, 0.01M in $NaClO_4$; B, 0.01M in NaCl; C, 0.01M in NaBr. Dotted lines, potential changed from — to + values. Curves A, B, and C were run after applying +0.6 V during 5 min before running, while curves A′, B′ and C′ were run after polarizing for 5 min at —1.5 V.

No detailed systematic study has been made in order to interpret the above observations. It appears that the electrode is covered with a film of oxide, even after cleaning in the EDTA-containing buffer. This is substantiated by the fact that anodization at +1 V after cleaning had no effect on the shape of the various current–potential curves. The depolarization by perchlorate, chloride and bromide ions might be attributed to a limited permeability of the film for these ions. Phosphate reacts with aluminum ions to form a slightly soluble compound, while EDTA forms a fairly stable complex with aluminum. Still, these ions do not depolarize anodically the aluminum electrode, which is accounted for by the assumption that the film is impervious to these ions. Similarly, the film seems to be impervious to oxygen.

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Hydroxyl and fluoride ions depolarize the electrode and it is concluded that the film is permeable to these ions. As an example, voltammograms of fluoride are given on $0.2M$ acetic acid and in $0.01M$ perchloric acid (Fig. 5). A diffusion current region is obtained and use of this can be made in the amperometric determination of fluoride in very dilute solutions. This will be discussed in more detail in a subsequent paper. Also the potential of the electrode is better defined in fluoride-containing solutions. This is evident from the fairly steep slope of the current–potential curve near the zero current potential.

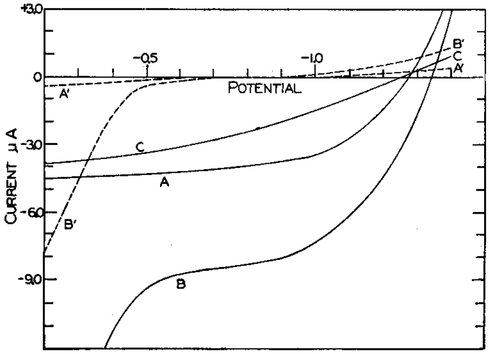

Fig. 5. Depolarization of the R.Al.E. by fluoride in various media. A, $4 \cdot 10^{-5}M$ NaF in $0.2M$ HAc; B, $7 \cdot 10^{-5}M$ NaF in $0.01M$ $HClO_4$; C, $4 \cdot 10^{-5}M$ NaF in $0.2M$ HAc after anodizing electrode for 2 h at 1 V. Dotted lines, A', B' are the residual currents in the supporting electrolytes alone.

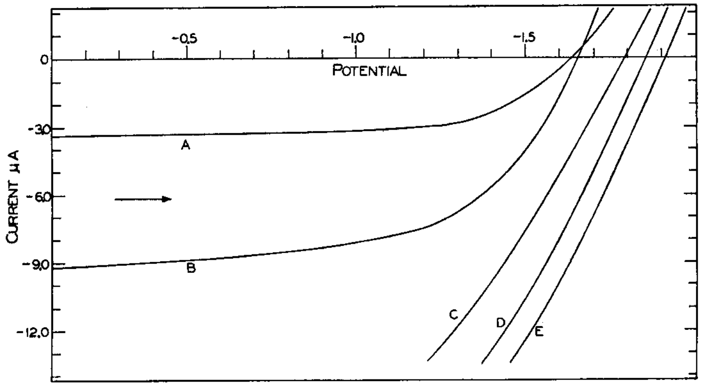

Fig. 6. Depolarization of electrode in alkaline medium. Voltammograms in air-free mixtures of $0.01M$ $NaNO_3$ and NaOH. Concentration of NaOH: A, $1 \cdot 10^{-4}M$; B, $2.6 \cdot 10^{-4}M$; C, $1.1 \cdot 10^{-3}M$; D, $0.01M$; E, $0.1M$.

After cleaning, the electrode was anodized in $0.2M$ acetic acid–$0.02M$ sodium acetate at +1 Volt for 2 h. Although the current was small, a film on the electrode was visible to the naked eye. This electrode was then placed in a $4 \cdot 10^{-5}M$ fluoride solution in $0.2M$ acetic acid and a voltammogram run (Fig. 5, curve C). Again a diffusion current region is observed, but the curve is much more drawn out than curve A, indicating that the heavier film on the electrode after anodizing exerts an interfering effect on the depolarization by fluoride, but is still permeable to fluoride ions.

Hydroxyl ions, like fluoride ions, depolarize the electrode anodically. Some typical voltammograms in sodium hydroxide solutions of varying strength are shown in Fig. 6. In dilute hydroxide solutions typical well defined diffusion current regions are observed (Fig. 6). Also, from the slopes of the curves at the zero current potential it is apparent that the electrode potential is fairly well defined in the presence of an excess of hydroxyl ions. Dilute solutions of sodium carbonate yield current-potential curves similar to those observed in dilute sodium hydroxide solutions.

Potential measurements

Potentials of the R.Al.E. in solutions of pH values ranging from 1.1 to 13 were determined in the presence and absence of air. The electrode was first cleaned in the EDTA solution and potentials were measured in the various solutions in the order from pH 1 to pH 7. After a constant potential had been attained, the electrode was rinsed with distilled water before the next measurement. After the measurement in the solution of pH 7 the electrode was cleaned in EDTA and potentials were measured in alkaline solutions in the order from pH 13 to pH 9. Potential readings were made at 2 min intervals and the electrode was considered to have attained the stationary potential when the reading did not change in a 5 min period. The pH was measured after the equilibrium potential had been determined. Results are shown in Table I. In acid medium (0.1*M* perchloric acid, 0.1*M* hydrochloric acid, 0.1*M* acetic acid, 0.1*M* acetic acid–0.1*M* sodium acetate) potential readings were irregular and reproducibility was very poor. The reported values are average potentials. Dependent on the previous history of the electrode, the potential was found to fluctuate in acid medium between —0.6 and —0.9V (*vs.* S.C.E.). Time required to attain stationary values varied from 10 to 82 min in these media. Once the stationary potential had been attained a change of pH in the solution did not affect the potential, indicating that the electrode does not function as a pH electrode in acid media. In acid air-saturated solutions the initial potentials were about 0.2 V more positive than in the absence of air, but the poorly defined stationary potentials slowly approached the same values. In oxygen-free alkaline solutions with a pH greater than 10 the equi-

TABLE I

POTENTIALS (IN V *vs.* S.C.E.) IN SOLUTIONS OF VARIOUS pH IN THE ABSENCE OF AIR

Electrolyte	*pH*	$-E$
0.1*M* $HClO_4$	1.10	0.6–0.8
0.1*M* HAc	2.87	0.6–0.8
0.1*M* HAc–0.1*M* NaAc	4.62	0.6–0.9
0.1*M* $NaNO_3$	6.9	0.8–0.9
0.1*M* Borax	9.2	1.576
0.05*M* Na_2CO_3 + 0.05*M* $NaHCO_3$	10.0	1.692
0.001*M* Borax + 0.05*M* Na_2CO_3	11.0	1.776
0.01*M* NaOH	(12.2)[a]	1.845
0.1*M* NaOH	(13.2)[a]	1.912
1*M* NaOH	(14.2)[a]	1.975

[a] not measured

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librium potential was established almost instantaneously and the potential was reproducible within 5 mV. Oxygen affects the potential of the electrode in alkaline solutions making it less negative. For example, the stationary potential of 0.1*M* borax in nitrogen was —1.576 V but in oxygen saturated solution —1.340 V. In 0.01*N* sodium hydroxide the values were —1.847 and —1.676 V respectively. The oxygen effect will be discussed further in a subsequent paper.

In the pH range between 11 and 14 the potential of oxygen-free solutions was found to change as an average 66 mV per unit change in pH. Assuming that the reaction.

$$Al + 4OH^- \rightleftharpoons H_2AlO_3^- + H_2O + 3e$$

is reversible and that the system remains saturated to the oxide, a standard potential ($[OH^-] = 1$) of —1.97 V (*vs.* S.C.E.) is calculated from the data in Table I. LATIMER[1] calculated a value of —2.31 V (*vs.* N.H.E.) or —2.55 V (*vs.* S.C.E.). Our value is about 0.6 V less negative than the calculated figure, but it is in good agreement with PLUMB's data[4].

As mentioned in the previous section, fluoride ions depolarize the electrode in acid media. As it is evident from the data in Table II, even a trace of fluoride ($2 \cdot 10^{-5}M$ has a profound effect on the potential of the aluminum electrode. Potentials are of the order of 300 to 600 mV more negative than in the absence of fluoride and they are reproducible within 10 mV. Oxygen shifts the potential to less negative values. In acid medium the potential changes only about 10 mV per unit change in pH, while at a pH greater than 10 the potentials are practically the same as those in the absence of a trace of fluoride. A more detailed account of the effect of the concentration of fluoride upon the electrode potential will be given in a subsequent paper in connection with a discussion of the potentiometric determination and titration of fluoride.

TABLE II

POTENTIALS (IN V *vs.* S.C.E.) IN SOLUTIONS CONTAINING $2 \cdot 10^{-5}M$ FLUORIDE

Electrolyte	*pH*	$-E$
0.1*M* $HClO_4$	1.2	1.236
0.01*M* $HClO_4$	2.1	1.247
0.1*M* HAc	2.9	1.253
0.1*M* HAc–0.1*M* NaAc	4.62	1.271
0.1*M* NaAc	8.2	1.543
0.01*M* NaOH		1.847
0.1*M* NaOH		1.912

From the present study it is evident that the aluminum electrode functions as a hydroxyl ion indicator electrode at a pH greater than 9 and as a fluoride ion indicator electrode in acid medium.

ACKNOWLEDGEMENT

Acknowledgement is made to the Graduate School of the University of Minnesota for financial support of this research.

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SUMMARY

A rotated aluminum wire electrode (R.Al.E.) is described for the determination of voltammograms and potentials. An aluminum electrode is highly polarizable both cathodically and anodically. Of all ions tested only hydroxyl and fluoride ions depolarize it anodically at highly negative potentials. In the absence of fluoride it is not a pH electrode, but it is a pOH electrode in the presence of an excess of hydroxyl ions. Fluoride in acid medium and hydroxyl ions yield well defined anodic diffusion currents. In the absence of fluoride or of an excess of hydroxyl ions the potential is ill defined. In acid medium a trace of fluoride ($2 \cdot 10^{-5} M$ or 0.4 p.p.m.) causes the potential to become approximately 600 mV more negative than in the absence of fluoride. At a pH greater than 11 the potential varies 66 mV per unit change of pH.

RÉSUMÉ

Une électrode tournante d'aluminium est décrite pour la détermination de ,,voltammogrammes" et de potentiels. Une électrode d'aluminium est très polarisable soit cathodiquement, soit anodiquement. De tous les ions essayés, seuls les ions hydroxyles et fluorures la dépolarisent anodiquement à des potentiels fortement négatifs. C'est une électrode de pOH en présence d'un excès d'ions OH^-. Les fluorures, en milieu acide et les ions hydroxyles donnent des courants de diffusion anodiques bien définis. En l'absence de fluorure ou d'un excès d'ions hydroxyles, le potentiel est mal défini.

ZUSAMMENFASSUNG

Es wird eine rotierende Elektrode aus Aluminium für die Bestimmung von ,,Voltagramme" und Potentialen beschrieben. Eine Aluminiumelektrode ist sowohl anodisch als auch kathodisch stark polarisierbar. Von allen untersuchten Ionen wird sie nur durch OH-Ionen und Fluorid-Ionen anodisch depolarisiert bei stark negativem Potential. Sie wirkt als pOH Elektrode in Gegenwart eines Überschusses von OH-Ionen. Fluoride in saurem Milieu und OH-Ionen geben gut definierte anodische Diffusionsströme. Bei Abwesenheit von Fluorid oder wenn zu wenig OH-Ionen zugegen sind, ist das Potential nicht eindeutig.

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SOLVENT EXTRACTION OF ANTIMONY(V) WITH ETHYL ACETATE

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In the course of an investigation on metal antimonates, it was found that by extraction with ethyl acetate, moderate amounts of antimony (V) could be quantitatively separated from Pb(II), Sn(IV), Ni(II), Cr(III) and Hg(II) in 6 *N* HCl. Extraction of antimony(V) either as the rhodamine-B chlorantimonate[1] or the citrate–oxalate complex[2] with ethyl acetate has been reported; these methods, however, are limited to trace determinations. The proposed method is applicable for the extraction of moderate amounts (0.05 to 0.2) of antimony(V) and is much simpler and more rapid. Lead(II), tin(IV), mercury(II), nickel(II) and chromium(III) are non-interfering. Moderate amounts of copper(II) similarly have no effect; but iron(III), tin(II), cadmium(II) and cobalt(II) are co-extracted and must be removed. The method has been successfully used for the determination of antimony in Pb, Sn, Ni, and/or Hg antimonates and for the analysis of type metal.

REAGENTS

Antimony stock solution

Approximately 32 ml of $SbCl_5$ (B.D.H. reagent grade) was dissolved in 250 ml of standard 6 *M* HCl. The solution was filtered through glass wool to remove suspended impurities and stored in a closed bottle provided with a semi-micro delivery burette. Definite volumes of the solution were removed and their antimony content determined iodometrically[3].

Hydrochloric acid stock solution

AnalaR HCl was diluted to 6 *M* and accurately standardized.

Ethyl acetate

Reagent grade, redistilled.

Standard decinormal thiosulphate solution

AnalaR sodium thiosulphate was dissolved in distilled water to make a *N*/10 solution. It was standardized against AnalaR potassium dichromate.

Other salts used were either B.D.H. AnalaR grade or Mercks pure reagents.

PRELIMINARY INVESTIGATION

Before attempting the actual separation of antimony from interfering elements, the effects of HCl concentration and Sb concentration on the extraction were examined. Preliminary extractions were carried out with a 1.0 *M* $SbCl_5$ solution in conc. (11.6 *N*) HCl. It was observed that extraction does not substantially increase above 6 *N* HCl, but when extractions were carried out with solutions more concentrated than 6 *M* in HCl, considerable reduction in volume of the ethyl acetate layer occurs. The volume reduction was nearly 50% with 8 *N* HCl, 60% with 10 *N* HCl and with 11.6 *N* HCl, no separation of the two layers were observed. Difficulties were also encountered in maintaining constant acidities of these solutions. Therefore, for the subsequent study a solution of $SbCl_5$ (1.0 *M* app.) in 6 *N* HCl was used.

EXPERIMENTAL PROCEDURE

The experimental solutions used for extraction were prepared by mixing together varying amounts of the antimony(V) stock solution, standard 6 *N* HCl and distilled water. The total volume was always 10 ml and contained known amounts of antimony(V) in the presence of varying amounts of HCl. The HCl content was calculated by assuming the antimony(V) stock solution to be 6 *M* in HCl. These solutions were extracted with an equal volume of ethyl acetate in a graduated syringe extractor[4] for 1 min. On the separation of the two layers, the phase volume was read and the organic layer removed. This was treated with 25 ml HCl and kept for some time until a homogenous phase resulted upon the addition of water. This solution was analysed for antimony by the iodometric method[3].

RESULTS AND DISCUSSION

Effect of HCl concentration

The effects of varying the HCl concentration on the extraction are given in Table I. It is immediately clear that high acidity is essential for satisfactory extraction. With solutions lower than 3.0 *M* in HCl, antimony(V) immediately hydrolyses and after

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shaking with ethyl acetate it is difficult to separate the two layers; the extent of extraction is, in addition, quite low (less than 30%) although, there is no appreciable reduction in the volume of the solvent. With stronger acid solutions, no hydrolysis occurs and the extraction continuously increases; however, there is a reduction in the volume of the solvent. As has been previously pointed out, higher acidities do not improve the extraction in any way. 6 *N* HCl solutions appeared to be most suitable since the extraction is considerable (87%) and the reduction in the volume of the solvent is little.

TABLE I

EXTRACTIBILITY OF ANTIMONY(V) BY ETHYL ACETATE AS INFLUENCED BY THE STRENGTH OF HCl

Antimony taken for each extraction 0.1128 g		
Molarity of HCl	*Final volume of organic layer ml*	*Percentage extraction*
6.00	8.0	87.48
5.97	8.0	86.42
5.97	8.0	85.88
5.97	8.0	86.96
5.82	8.0	84.82
5.82	8.0	85.35
5.73	8.0	84.03
5.73	8.0	84.82
5.67	8.0	83.75
5.67	8.0	84.82
5.37	8.0	80.02
5.37	8.0	81.65
5.08	8.0	81.70
5.08	8.0	81.65
4.78	8.0	71.22
4.78	8.0	68.28
4.18	8.5	53.34
4.18	8.5	54.68
3.58	9.0	36.00
3.58	9.0	42.68
2.99	9.5	27.20[a]
2.69	9.5	28.80[a]
2.39	10.0	26.68[a]
2.09	10.0	29.34[a]

[a] Hydrolysis takes place

Effect of antimony(V) concentration

The effect of antimony(V) concentration on extraction was subsequently examined. Keeping the acidity (HCl) and volume of the solution identical with that found optimum in previous experiments, only the antimony content was varied between such limits as appeared suitable for rapid and accurate volumetric estimation. Results are given in Table II. It will be noted that a four-fold change in metal concentration produces but little effect. A slight improvement in extraction is noted with increasing antimony concentration.

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Distribution coefficient of Sb(V) under optimum conditions

The distribution coefficient of antimony under optimum conditions was next determined by extracting 5, 10 and 15-ml portions of solutions containing (1.0007 g) Sb(V) in 6 *N* HCl. The average value corresponds to 6.56 at 25–28°. It is obvious that 3 extractions will quantitatively separate the antimony(V).

TABLE II

PERCENTAGE EXTRACTION WITH DIFFERENT AMOUNTS OF ANTIMONY

Antimony taken *g*	*Percentage extractions*
0.0564	85.63
0.1128	87.48
0.1692	88.51
0.2256	91.47

Behaviour of other interfering ions

Under optimum conditions, iron(III) is completely co-extracted while tin(II), cadmium(II) and cobalt(II) are moderately extracted. Moderate amounts (0.0167 to 0.05 g) of copper(II) have no effect but larger amounts introduce a positive error.

TABLE III

RESULTS FOR ANTIMONY(V) IN THE PRESENCE OF INTERFERING ELEMENTS

Element	*Amount added* *g*	*Added as*	*Antimony taken* *g*	*Antimony found* *g*	*Difference* %
Nickel	0.05	$NiSO_4 \cdot 7\ H_2O$	0.1007	0.1007	0.0
	0.10	,,	0.1007	0.1001	—0.6
	0.15	,,	0.1007	0.1007	0.0
Chromium	0.05	$CrK(SO_4)_2 \cdot 12\ H_2O$	0.1007	0.1007	0.0
	0.10	,,	0.1007	0.1001	—0.6
	0.15	,,	0.1007	0.1001	—0.6
Lead	0.10	$Pb(OOCCH_3)_2 \cdot 3\ H_2O$	0.1007	0.1001	—0.6
	0.90	,,	0.1007	0.0999	—0.8
Tin	0.05	$SnCl_2 \cdot 2\ H_2O$, oxidized with $KClO_3$	0.1013	0.1007	—0.6
	0.10	,,	0.1013	0.1013	0.0
	0.15	,,	0.1013	0.1013	0.0
Copper	0.0167	$CuSO_4 \cdot 5\ H_2O$	0.1013	0.1007	—0.6
	0.0333	,,	0.1013	0.1019	+0.6
	0.0500	,,	0.1013	0.1019	+0.6
	0.1000	,,	0.1013	0.1030	+1.7
	0.1500	,,	0.1013	0.1061	+4.8
Mercury	0.05	$HgCl_2$	0.1037	0.1024	—1.3
	0.10	,,	0.1037	0.1042	+0.5
	0.15	,,	0.1037	0.1042	+0.5
Tin and lead	0.10 g Sn(IV)	$SnCl_2 \cdot 2\ H_2O$ oxidized with $KClO_3$	0.1007	0.1006	—0.1
and	0.90 g Pb(II)	$Pb(OOCCH_3)_2 \cdot 3\ H_2O$			
Type metal[a]			0.1400	0.1403	+0.3

[a] Type metal containing 14% Sb, 81% Pb, 5% Sn.

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Determination of antimony in the presence of other elements

Determination of antimony in synthetic mixtures with other elements was carried out by 3 extractions with ethyl acetate from 6 *N* HCl. Results are given in Table III and indicate that the method is quite suitable for the rapid determination of antimony(V) in the presence of Pb(II), Sn(IV), Ni(II), Cr(III) and Hg(II). Maximum deviation is within ± 1%.

RECOMMENDED PROCEDURE FOR ANTIMONATES AND TYPE METAL

Method for antimonates

Decompose 0.25 g of antimonate with 15 ml conc. HCl in a casserole. Boil down to 5 ml, add 5 ml conc. HCl, and after cooling, dilute with an equal volume (10 ml) of distilled water. Transfer the clear solution to a syringe extractor. Wash the casserole with 20 ml of ethyl acetate and draw the solvent into the extractor. Extract for 1 minute, allow for separation and remove the solvent layer. Add 20 ml of fresh ethyl acetate to the casserole and draw again into the extractor. Repeat the extraction once more (3 times in all). Treat the combined extracts with 25–30 ml conc. HCl and heat gently until a homogeneous solution results up on the addition of water. Dilute to 20% v/v HCl with water. Add 2–3 g KI and titrate the liberated iodine with standard *N*/10 thiosulphate in the usual way.

Method for type metal

Treat 1 g of type metal with 20 ml conc. HCl containing 2 ml bromine (liquid). Towards the end of the reaction heat gently until solution is complete. Add 10 ml of 20 vol. hydrogen peroxide and boil to completely remove bromine. Evaporate to near dryness and add 10 ml of conc. HCl. After cooling, dilute with 10 ml of distilled water. Subject the solution to extraction with ethyl acetate in the same fashion as given above for antimonates.

SUMMARY

A method has been derived for the selective extraction of antimony(V) from hydrochloric acid solution with ethyl acetate. The method can be employed for the rapid determination of antimony in antimonates of lead, tin, mercury, nickel and chromium and in type metal. Iron(III), cobalt(II) cadmium(II), and large amounts of copper(II) and tin(II) interfere with the extraction. For the analysis of type metal, tin must be oxidized to the tetravalent state.

RÉSUMÉ

Une méthode est proposée pour l'extraction sélective de l'antimoine(V), en solution chlorhydrique, au moyen d'acétate d'éthyle. Ce procédé permet un dosage rapide de l'antimoine en présence de plomb, d'étain(IV), de mercure, de nickel et de chrome. Par contre, le fer(III), le cobalt, le cadmium et de grandes quantités de cuivre et d'étain(II) gênent.

ZUSAMMENFASSUNG

Antimon lässt sich aus salzsaurer Lösung mit Aethylacetat selektiv extrahieren. Diese Methode erlaubt eine rasche Bestimmung von Antimon neben Blei, Zinn-(4), Quecksilber, Nickel und Chrom. Störend wirken Eisen-(3), Kobalt, Cadmium sowie grössere Mengen von Kupfer und Zinn-(2).

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HIGH FREQUENCY TITRATION AND ESTIMATION OF IONS

I. DETERMINATION OF BARIUM, LEAD, THALLIUM, CALCIUM, CERIUM, COPPER AND SILVER

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Recently MAJUMDAR AND MUKHERJEE[1] have estimated silver volumetrically with various organic and inorganic reagents using high frequency titrimetry. The utility of this technique has been widely illustrated by the authors in the present paper. A number of different metal ions has been estimated with standard solutions of chromate, oxalate and ferrocyanide and the accuracy has been found to be no less than that obtained with classical gravimetric or volumetric methods. The only difficulty observed is that with high ionic concentration, the end-point is not sharp enough, due perhaps to the low frequency of the crystal (6 Mc) used in the instrument.

The high frequency technique is only a special form of conductometry. However, absence of contact between the electrodes and the solution eliminates errors caused by coating of the electrodes by a precipitate and other surface phenomenon. The general applicability of the high frequency method to precipitation titrations[2-4] suggests an investigation of the new volumetric technique for the determination of elements using a high frequency oscillator for end-point detection.

EXPERIMENTAL

Apparatus and chemicals

The apparatus used is identical with that reported in a previous paper[1].

The chemicals and the reagents used were all of A.R. quality.

Lead, barium and thallium(I) were estimated with standard potassium chromate solution.

Although a number of methods have been developed for their determinations, the number of good volumetric procedures is limited. The ordinary methods for the determination of these elements involve precipitation by chromate solution and determination of the iodine evolved on their reaction with potassium iodide. KOLTHOFF AND PAN[5] have described an amperometric method for the determination of lead with dichromate as the titrant. High frequency titration of these elements by chromate is greatly simplified and the time required for each titration is much less than the ordinary volumetric procedure.

Procedure

A measured volume of the solution to be analysed was taken in the titration cell which consisted of a 100-ml beaker with two metal rings on its outside surface. Since about 70 ml of the solutions were required to cover the rings, all titrations were carried out with this amount as the initial volume. The solution, after dilution to the required volume, was titrated with the standard solution of chromate, after the high frequency instrument was tuned to resonance (maximum power absorption by the cell solution) with the tuning condenser. The course of the titration is followed exactly in the same manner as previously reported[1]. The titration curves, obtained by plotting the change in dial reading per volume increment of the titrant, against the volume of the titrant, are shown in Fig. 1.

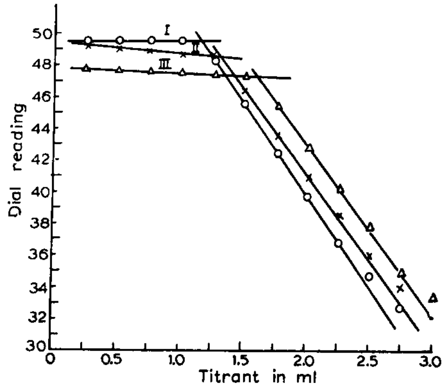

Fig. 1. I. Titration of $1.71 \cdot 10^{-2}M$ Pb^{+2} by $3.534 \cdot 10^{-2}M$ K_2CrO_4.
II. Titration of $1.851 \cdot 10^{-2}M$ Ba^{+2} by $3.530 \cdot 10^{-2}M$ K_2CrO_4.
III. Titration of $2.291 \cdot 10^{-2}M$ Tl^{+} by $3.534 \cdot 10^{-2}M$ K_2CrO_4.

The results of analysis are presented in Table I. An accuracy of about ±1% was observed for the majority of the cases. In the case of lead, the pH of the solution was kept between 5.0 to 6.5, and at this pH, lead up to 20 mg was estimated. For barium, the pH of the solution was kept between 6.0 to 6.5 when up to 20 mg of the metal was determined. Presence of calcium and magnesium, up to a maximum concentration of 5 mg (Ba, 10 mg), does not interfere. Thallium(I), when present up to a maximum concentration of 50 mg, was estimated at a pH between 6–6.5.

TABLE I

Metal taken mg	*Found mg*	*Deviation*
Pb 3.54	3.51	—0.03
8.86	8.79	—0.07
17.72	17.73	+0.01
Ba 6.35	6.30	—0.05
12.70	12.60	—0.10
19.0	18.9	—0.10
Tl 4.68	4.64	—0.04
23.41	23.20	—0.21
46.82	46.44	—0.38

Estimation of calcium and cerium by ammonium oxalate

Calcium and cerium(III) were determined by direct titration with a standard solution of ammonium oxalate in presence of 30% (v/v) of ethyl alcohol. In the absence of alcohol, precipitation of calcium and cerium oxalates was found to be slow and hence the detection of their end-points was rather difficult.

By this method, calcium up to 10 mg was estimated at a pH near 5.5. Accurate determination of Ce(III) by oxalate was possible only when the cerium content was between 10 and 40 mg. At lower concentrations, errors were high probably due to the slow coagulation of the precipitate. Ce(III), if present in very small amounts, could be estimated by adding to it a known excess and then titrating; the actual cerium content was then found by difference. Results are shown in Table II (Fig. 2).

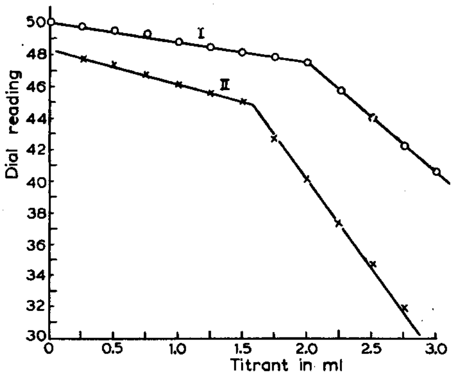

Fig. 2. I. Titration of $4.021 \cdot 10^{-2} M$ Ca^{+2} by $5.00 \cdot 10^{-2} M$ $(NH_4)_2C_2O_4$. II. Titration of $2.565 \cdot 10^{-2} M$ Ce^{+3} by $6.819 \cdot 10^{-2} M$ $(NH_4)_2C_2O_4$.

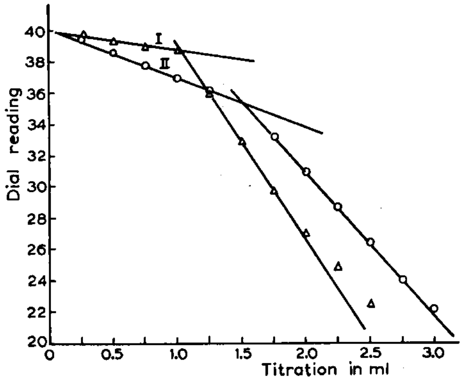

Fig. 3. I. Titration of $1.697 \cdot 10^{-2} M$ Ag^{+} by $2.015 \cdot 10^{-2} M$ $K_4Fe(CN)_6$. II. Titration of $2.447 \cdot 10^{-2} M$ Cu^{+2} by $2.16 \cdot 10^{-2} M$ $K_4Fe(CN)_6$.

TABLE II

Metal taken mg		*Found mg*	*Deviation*
Ca	4.02	4.00	—0.02
	8.04	8.01	—0.03
Ce	10.26	10.20	—0.06
	20.52	20.48	—0.04
	41.04	40.84	—0.20

TABLE III

Metal taken mg		*Found mg*	*Deviation*
Cu	3.88	3.84	—0.04
	7.76	7.70	—0.06
Ag	9.15	9.12	—0.03
	18.30	18.25	—0.05

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Estimation of copper(II) and silver(I) by ferrocyanide

The estimation of copper(II) and silver (I) was carried out with a standard solution of potassium ferrocyanide at a pH between 5.0 to 6.5. The maximum amount of copper that could be tolerated was only 10 mg whereas silver was determined even when present in a concentration of 20 mg. Results are given in Table III (Fig. 3).

ACKNOWLEDGEMENTS

Our grateful thanks are due to the University Grants Commission, Government of India, for providing us with the funds for the construction of the high frequency titration apparatus.

SUMMARY

Solutions of potassium chromate, ammonium oxalate and ferrocyanide are used as titrants for the high frequency titration of metal ions. Lead and barium, up to 20 mg, and thallium, up to 50 mg, are estimated with chromate and yield good results. Similarly, ammonium oxalate behaves satisfactorily when the concentration of calcium is not more than 10 mg and that of cerium is between 10 and 40 mg. Copper and silver can be titrated by ferrocyanide only up to a concentration of 10 and 20 mg, respectively. In all cases, the pH of the solution should preferably be between 6.0 and 6.5, though it can be extended in some cases to as low as 5.0.

RÉSUMÉ

Le chromate de potassium, l'oxalate d'ammonium et le ferrocyanure de potassium peuvent être utilisés comme réactifs pour les titrages à haute fréquence du plomb, du baryum et du thallium (avec chromate); du calcium et du cérium (avec oxalate); du cuivre et de l'argent (avec ferrocyanure).

ZUSAMMENFASSUNG

Es werden Methoden zur Hochfrequenztitration von Metall-Ionen beschrieben. Für die Bestimmung von Blei, Barium und Thallium wird eine Kaliumchromatlösung, für Calcium und Cerium eine Ammoniumoxalatlösung und für Kupfer und Silber eine Kaliumferrocyanidlösung verwendet.

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TARTRAZINE, A NEW SELECTIVE REAGENT FOR ZIRCONIUM

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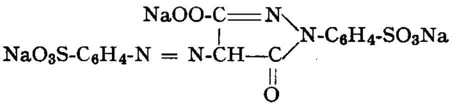
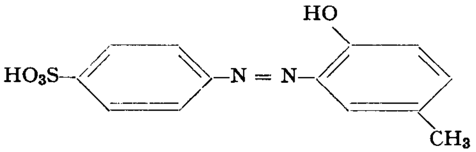
A critical survey of gravimetric methods for zirconium by means of organic reagents shows that few methods permit direct weighing of the precipitate; among them the 8-hydroxyquinoline[1] and mandelic acid[2] methods are the most promising. Owing to the inhomogeneous composition of the precipitates the final weighing form is generally zirconium oxide. In the present paper a new reagent for precipitation of zirconium(IV) is proposed, namely tartrazine:



This reagent was chosen on the basis of the observations made by KUZNETSOV[3] who examined monoazo dyes and found that the compounds formed in some cases are difficultly soluble precipitates of zirconium and hafnium. The presence of substituting groups in the molecule of the monoazo dyes has a great influence on the properties of the final products. Of particular value is the effect of a hydroxyl group in the *ortho* position adjacent to the azo group.

Another compound which is a very good reagent for zirconium is 2-hydroxy-5-methylazobenzene-4′-sulfonic acid.



Tartrazine contains a carboxylic group situated near to the azo group. This substance reacts in slightly acidic solutions with the salts of zirconium(IV), forming a yellow–orange precipitate. The insolubility of this precipitate in water encouraged us to examine its possibilities for the determination of zirconium.

EXPERIMENTAL

To a zirconium salt solution (nitrate or oxychloride), the concentration of which had been determined by precipitation with ammonium hydroxide and calcination as oxide, an aqueous 2% solution of tartrazine* was added dropwise until precipitation

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* The reagent solution used was previously filtered. The reagent is a product of a "Colorom Codlea" factory.

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was complete. The pH of the precipitation was 1; but precipitation was also complete in stronger acid medium. The mixture was then heated to 60–80° and filtered through a blue band filter paper. The precipitate was washed with distilled water till the colour of the filtrate became very slight yellow and then calcined to the oxide.

The results obtained are recorded in Table I.

TABLE I

Volume of $ZrOCl_2$ solution ml	*Zr calculated g*	*Zr found g*	*Zr difference mg*
5	0.0050	0.0050	± 0
10	0.0100	0.0099	— 0.1
10	0.0100	0.0100	± 0
10	0.0100	0.0100	± 0
12.5	0.0125	0.0126	+ 0.1
12.5	0.0125	0.0125	± 0
15	0.0150	0.0150	± 0
20	0.0200	0.0200	± 0
25	0.0250	0.0249	— 0.1
30	0.0300	0.0298	— 0.2

Filtration on an A_2-filter crucible was next attempted; the precipitate was dried at 110° for 1 h, and then weighed.

The results obtained are shown in Table II.

TABLE II

Volume of $ZrO(NO_3)_2$ solution ml	*Complex g*	*Zr calculated g*	*Zr found g*	*Zr difference mg*
5	0.0171	0.0055^8	0.0055^8	± 0
5	0.0169	0.0055^8	0.0055^2	— 0.06
10	0.0342	0.0111^6	0.0111^7	+ 0.01
10	0.0340	0.0111^6	0.0111	— 0.06
15	0.0513	0.0167^4	0.0167^5	+ 0.01
15	0.0510	0.0167^4	0.0166^5	— 0.09
20	0.0684	0.0223^2	0.0223^8	+ 0.01
20	0.0680	0.0223^2	0.0222	— 0.12

The factor, 0.32653, corresponds to the formula Zr_3 (tartrazine) $(OOH)_3$.

The results obtained show that the method of precipitation of zirconium with tartrazine is one of the few methods which allows direct weighing of the precipitate.

The specificity of the reagent

Qualitative tests were made of interferences of a series of ions and the following results were obtained.

a. Ions which do not react with tartrazine: aluminium, titanium, uranyl, lanthanum, cerium, potassium, cadmium, zinc, cobalt, nickel, copper, magnesium, sodium,

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lithium, iron, calcium; tests were made especially with those elements which accompany zirconium in alloys and ores.

b. Ions which react with tartrazine giving precipitates or opalescences, which disappear after adding hydrochloric or nitric acid; barium solutions when heated become opalescent, thorium in neutral solution forms a yellow precipitate which dissolves in acid, and mercuric ions form an orange precipitate soluble in nitric acid.

c. The reaction is masked by sulfate and by tartaric or citric acid.

We propose to apply the method to the analysis of alloys and ores.

SUMMARY

A new method for determining zirconium is described, in which tartrazine serves as reagent. The precipitate can be ignited to ZrO_2 or weighed as the complex. The reagent appears to be very selective, and can be used for the determination of zirconium in alloys and ores.

RÉSUMÉ

Une nouvelle méthode est proposée pour le dosage gravimétrique du zirconium au moyen de tartrazine. Grâce à sa bonne spécificité, ce procédé peut être appliqué à des analyses d'alliages et de minerais.

ZUSAMMENFASSUNG

Es wird eine neue Methode beschrieben zur gravimetrischen Bestimmung von Zirkon mit Tartrazin. Da die Reaktion sehr specifisch ist, eignet sie sich zur Bestimmung von Zirkon in Legierungen und Mineralien.

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SPECTROPHOTOMETRIC DETERMINATION OF GOLD WITH PHENYL-α-PYRIDYL KETOXIME

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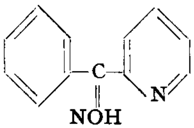
Phenyl-α-pyridyl ketoxime (I) was previously reported as a chelating agent[1] and



(I)

was used for the spectrophotometric determination of palladium[2]. This reagent formed a water insoluble, orange-yellow precipitate with gold(III) which was soluble in chloroform. The present paper describes a procedure for the spectrophotometric determination of gold using phenyl-α-pyridyl ketoxime as the reagent.

The spectrophotometric methods for the determination of gold are relatively few. The spectrophotometric method for the estimation of gold based on the formation of colloidal gold is subject to numerous variables[3]. Both the bromoaurate[4] and the rhodanine[5] methods suffer from interference by the metals with which gold is very frequently associated. Leuco malachite green and *o*-tolidine are oxidized by gold(III) to produce colored oxidation products. These colored substances have been used for the spectrophotometric determination of gold[6,7]. Recently, MacNulty and Woollard[8] used the rhodamine B method for the estimation of very small amounts of gold.

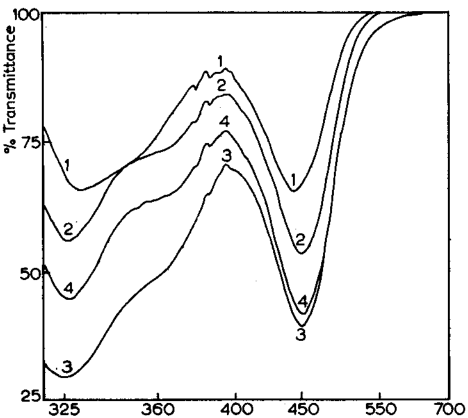


Fig. 1. Spectral curves of gold(III) phenyl-α-pyridyl ketoximate. Gold concentration: 8 p.p.m.; Cell thickness: 1 cm. (1) pH 1.7, (2) pH 2.5, (3) pH 3.2, (4) pH 4.1.

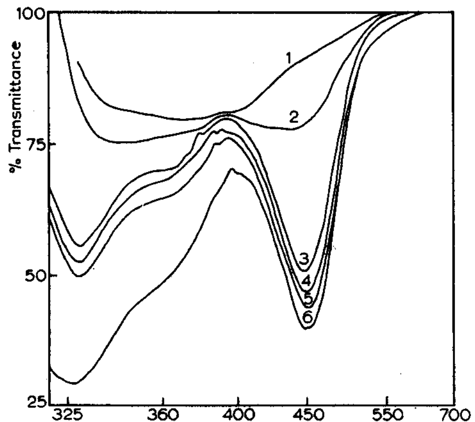


Fig. 2. Spectral curves of gold(III) phenyl-α-pyridyl ketoximate. (1) pH 11.5, (2) pH 10, (3) pH 9.1, (4) pH 7.0, (5) pH 6.0, 5.3, (6) pH 3.2.

Gold(III) reacted with phenyl-α-pyridyl ketoxime to produce a water insoluble chelate. The product was crystalline, orange-yellow in color, and dissolved in chloroform to give a yellow solution. The chloroform extract showed a very sharp light absorption peak at 450 mμ. There was also another absorption band in the ultraviolet region (Figs. 1 and 2). Spectrophotometric determinations were made at 450 mμ because in this region the absorption peak was very sharp and there was also no absorption by the reagent.

EXPERIMENTAL

Spectral studies and light absorbance measurements were made with a Beckman Model DK-1 recording spectrophotometer and a Beckman Model DU spectrophotometer. Matched silica cells of 1-cm light path were used. pH measurements were made with a Beckman Model G pH meter.

Reagent solution. A 1-% solution of phenyl-α-pyridyl ketoxime in 95% ethanol was used as the reagent.

Standard solutions. All chemicals used were of reagent grade.

Gold. The gold solution was prepared from gold(III) chloride; it was 1*M* with respect to hydrochloric acid. The solution was standardized by precipitating the gold with hydroquinone and weighing as metal according to Beamish[9].

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The solutions of other cations were prepared from their sulfates, chlorides, and nitrates. Their strengths were determined by standard procedures. The osmium solution was prepared by starting with osmic acid. The solutions of the anions were prepared from their potassium and sodium salts. The various buffer solutions were prepared according to VOGEL[10].

TABLE I

WAVELENGTHS OF LIGHT ABSORPTION PEAKES OF A NUMBER OF METAL PHENYL-α-PYRIDYL KETOXIMATES IN CHLOROFORM

Cation	*Wave-length of absorption peakes mμ*	*Remark*
Fe^{+2}	530	Absorption rapidly increases after 460 mμ
Co^{+2}		Absorption rapidly increases after 600 mμ
Ni^{+2}		Absorption rapidly increases after 550 mμ
Cu^{+2}	475 350	
Pd^{+2}	410 327	
Au^{+3}	450 325	

Light absorption spectrum of gold phenyl-α-pyridyl ketoximate and effect of pH on chelation and extraction

The spectral characteristics of the phenyl-α-pyridyl ketoximates of different cations were reported in an earlier communication[2]. Table I summarizes the regions of maximum absorption of the different chelates. The solutions for the present studies were prepared as follows: 200 μg (8 p.p.m. in the final solution) of gold were taken in a 50-ml beaker. 1 ml of the 1% reagent solution was then added to the gold solution followed by 2 ml of water. The pH of the solution was then adjusted with sodium carbonate or sodium bicarbonate solution and the pH was recorded with a pH meter. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water for washing the beaker. The volume of the solution was maintained approximately at 10 ml. The solution was then extracted three times with chloroform using 5 ml chloroform each time. The volume of the chloroform extract was made up to 25 ml with chloroform and the light transmittance of the chloroform extract was measured with a Beckman DK-1 spectrophotometer. The results are shown in Figs. 1 and 2. Any gold left in the aqueous phase was detected by applying the dimethylaminobenzylidenerhodanine spot test[11]. Prior to applying the spot test, the aqueous phase was evaporated almost to dryness and the organic reagent was decomposed by treating the residue with 5 ml aqua regia and evaporating to dryness. The treatment with aqua regia was repeated three times. The final residue was extracted with 5 ml of water. The spot test was carried out with this solution. No positive test for gold was given by the aqueous phase when the extractions were performed between pH 2.5 and 9.1. The spectral curves (Fig. 1 and 2) also indicated that the optimum pH for chelation and extraction was between 3 and 6. At pH 11.5 there was no chelation as was evidenced by the absence of the characteristic peakes.

Effect of the buffers

200 μg of gold (8 p.p.m. in the final solution) were taken in a 50-ml beaker. 1 ml of the reagent solution was then added to it followed by 3 ml of water. The pH of the solution was then adjusted between 3 and 9 by the addition of sodium carbonate or bicarbonate solution. 1 ml of the appropriate buffer solution was then added. Acetate, phosphate, borate, ammonia-ammonium chloride and tartrate buffers were used. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water to wash the beaker. The solution was then extracted three times with chloroform using 5 ml of chloroform each time. The volume of the chloroform extract was then made up to 25 ml with chloroform and the absorption spectrum of the chloroform extract was studied using a Beckman Model DK-1 spectrophotometer. Excepting the case when extraction was performed from the tartrate buffered system, in all cases the spectral characteristics of the chloroform extracts were exactly identical whether the extraction was performed from the buffered or the corresponding unbuffered solution of same hydrogen ion concentration. When the tartrate buffer was used there was a considerable decrease in absorbance all along the spectrum. This probably was due to the partial reduction of gold.

TABLE II

EFFECT OF REAGENT ON THE ABSORBANCE OF THE CHLOROFORM EXTRACT OF THE GOLD CHELATE

Amount of gold mg	*Amount of reagent mg*	*Amount of reagent / Amount of gold*	*Absorbance*
0.2	0.5	2.5	0.08
	1.0	5.0	0.14
	5.0	25.0	0.40
	10.0	50.0	0.40
	20.0	100.0	0.40
	50.0	250.0	0.38
	100.0	500.0	0.28

Effect of reagent, temperature, and time

The amount of gold used, the dilution, and the general procedure for extraction were the same as in previous studies. The pH of all the solutions was adjusted between 3.5 and 4.5 before the extraction and no buffer was used. During the study of the effect of the reagent, the amount of reagent added was varied (see Table II). During the study of the effect of temperature and time, 1 ml of the 1% reagent solution was used. The temperature of the chloroform extract between 0 and 45° was without any effect. There was no change in absorbance of the chloroform extract in two weeks. The color development was instantaneous. All absorbance measurements were made at 450 mμ and against proper blank solutions.

Beer's law

The gold solution and 2 ml of the reagent solution were taken in a 50-ml beaker, the solution was diluted to about 5 ml and the pH of the mixture adjusted between 3.5 and 4.5 by the addition of sodium bicarbonate solution. The solution was then transferred to a 50-ml separatory funnel using a minimum volume of water to wash the beaker. The solution was then extracted 3 times with chloroform using 5 ml of chloroform each time and the final volume of the chloroform extract was made up to 25 ml with chloroform and the absorbance measured at 450 mμ. All measurements were made against a blank prepared similarly except that it did not contain any gold. The results are shown in Table III.

TABLE III

STUDY OF BEER'S LAW

Amount of gold *µg*	*Concn. of gold p.p.m.*	*Absorbance*	*Specific absorptivity*[a]	*Mean specific absorptivity*
50	2	0.08	40.0	47.9
100	4	0.20	50.0	
150	6	0.28	46.6	
200	8	0.40	50.5	
250	10	0.50	50.0	
300	12	0.58	48.3	
350	14	0.70		
400	16	0.80	50.0	

[a] $$\text{Specific absorptivity} = \frac{\text{Absorbance}}{\text{mg of gold/ml} \times \text{cell thickness}}$$

Effect of diverse ions

Binary mixtures were prepared containing 200 μg of gold and 10 mg of a second cation. The mixture treated with 2 ml of the reagent solution. The subsequent steps in the procedure were the same as in the case of studying Beer's law. The absorbance of the chloroform layer was measured at 450 mμ. Alkaline earth metal ions, Ag^+, NH_4^+, Cd^{+2}, Pb^{+2}, Mn^{+2}, VO^{+2}, Al^{+3}, Bi^{+3}, Fe^{+3}, Ru^{+4}, Rh^{+3}, Os^{+4}, Ir^{+4} and Pt^{+4} did not interfere. The precipitate thrown down during the study, Ag^+, Bi^{+3}, and Fe^{+3}, separated at the interface of the two phases and was removed by dry filtration. Interference due to Cu^{+2}, Co^{+2}, and Ni^{+2} was eliminated by using 0.1*M* EDTA solution. During these studies the reference gold sample as well as the blank were treated with identical amounts of EDTA solution. The presence of EDTA decreased the absorbance of the gold chelate by about 5%. Pd (II), Hg^{+2}, Fe^{+2}, Cn^-, Br^-, I^- and the organic anions like oxalate, citrate and tartrate seriously interferred with the method.

Sensitivity

Limit of identification = 1 μg
Limit of dilution = 1:1,000,000

DISCUSSION

Phenyl-α-pyridyl ketoxime was found to be a sensitive reagent for the spectrophotometric determination of gold. There was no interference by the ions with

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which gold is usually associated. Beer's law was obeyed between 2 and 16 p.p.m. of gold. Under the present experimental conditions the optimum concentration range for a minimum photometric error was between 4 and 10 p.p.m. In the last column of Table III the specific absorptivity defined as

$$\frac{\text{Absorbance}}{\text{mg of gold/ml} \times \text{cell thickness}}$$

is given instead of the molar extinction coefficient. The present investigator is not yet certain whether gold and reagent combine in the ratio of 1 mole to 2 moles or 1 mole to 3 moles. In any case, the molar extinction coefficient will be of the order 10^4. The values of the specific absorptivity show a high reproducibility of the method. The results in Table II show that an amount of reagent between 5 and 250 times the amount of gold produces a maximum color intensity in the chloroform extract.

The results of the investigation about the structure of gold and other metal phenyl-α-pyridyl ketoximates and the other analytical applications of this reagent will be published in subsequent communications.

ACKNOWLEDGEMENT

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SUMMARY

A method is described for the spectrophotometric determination of gold in the concentration range of 2 to 16 p.p.m. using phenyl-α-pyridyl ketoxime as the reagent. The reagent permits to detect 1 μg of gold in 1 ml of a solution. The method is particularly free from interference by the ions with which gold is frequently associated.

RÉSUMÉ

Une méthode spectrophotométrique sensible et sélective est décrite pour le dosage de l'or. On utilise comme réactif l'oxime de la phényl-α-pyridylcétone.

ZUSAMMENFASSUNG

Es wird eine empfindliche und selektive spektrophotometrische Methode zur Bestimmung von Gold mit Hilfe von Phenyl-pyridyl-ketoxim beschrieben.

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DETERMINATION OF COPPER AND ZINC IN METALLURGICAL PRODUCTS BY AUTOMATIC DERIVATIVE SPECTROPHOTOMETRIC TITRATIONS

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The methods often used for the determination of copper and zinc in metallurgical products are quite time-consuming and many attempts have been made to shorten them. Complexometric titrations using ethylenediaminetetraacetic acid (EDTA) as titrant and metal indicators for visual end-point detection have been tested and have provided good results[1-6].

Recently the authors described an automatic titration method for the determination of Ca and Mg[7]. The subjective evaluation of end-points was eliminated by using the automatic derivative spectrophotometric end-point detection system provided in the new, commercially available "Spectro-Electro" titrator[8] (E. H. Sargent Co., Chicago, Ill.). The same titrator and spectrophotometric end-point detection system has been found to be well suited for the automatic titration of Cu and Zn in brasses and bronzes.

The Cu^{+2} in an aliquot of dissolved sample reacts with excess iodide at pH 4.0 and the liberated iodine is automatically titrated. The UV absorption band of iodine between 350 and 400 mμ provides an excellent end-point signal for termination of the titration[9]. Another aliquot of sample is also buffered at pH 4.0 and both Cu and Zn are automatically titrated with EDTA as titrant and 1-(2-pyridylazo)-2-naphthol (PAN) as indicator; the Zn is calculated by difference.

The automatic end-points are reproducible and accurate within 0.01 ml of 0.025M thiosulfate solution and 0.02 ml of 0.01M EDTA solution, and the results check closely with standard values. The total time required for a complete analysis of both Cu and Zn is about 20 min, including weighing, addition of reagents, separations, titrations and calculations. Interfering ions are removed by precipitation as the hydroxides in the presence of an excess of ammonium hydroxide.

APPARATUS

The Sargent-Malmstadt "Spectro-Electro" titrator was used[8]. The photoconductive detector circuit supplied with the titrator was connected according to instructions in the instrument manual.

Since two different titrants are required for the titrations, it is desirable to fix two delivery tips in correct position relative to the stirrer, and to connect the top end of each delivery tip to its respective buret tip with a short piece of gum rubber or neoprene tubing. Each tubing passes through a separate buret valve. A buret valve and suitable buret for each titrant are mounted on each of the two support rods.

A second buret valve and switching arrangement for selecting either titrant are not part of the standard equipment. However, another buret valve can be obtained and the switching device easily assembled. A diagram of the titrant switching system is shown in Fig. 1. The parts are mounted in a small 3$^1/_2$" × 2" × 2" aluminum box with the pilot lights and switch protruding through one side and the sockets available from the opposite side. The switch box is mounted between the two rods holding the two burets, and the valves for controlling delivery of the titrants are plugged into their proper outlets. A 3' cord connects the switch box to the valve outlet in the back of the Spectro-Electro titrator. The delivery of the proper titrant is determined by the position of the toggle switch marked "$Na_2S_2O_3$" in one position and "EDTA" in the other position.

A 5-ml buret, graduated in 0.01-ml divisions and equipped with delivery and refill teflon stopcocks and titrant reservoir was used for the $Na_2S_2O_3$ titrant and a 10-ml self-zeroing buret also equipped with delivery and refill teflon stopcocks and titrant reservoir was used for the EDTA titrant. Both burets are products of Fischer-Porter Co. (Hatboro, Pennsylvania).

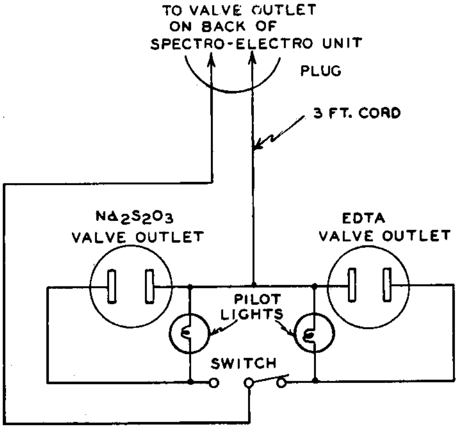

Fig. 1. Titrant selector.

REAGENTS

Standard $10^{-2}M$ *copper solution.* Dissolve 0.6354 g reagent grade copper sheet in slight excess of concentrated HNO_3 and dilute to the mark in 1-l volumetric flask with deionized water. 1 ml contains 0.6354 mg copper.

Zinc solution. Dissolve 0.6538 g of reagent grade zinc (Grannular, 20 mesh) in 1:1 HCl and dilute up to 1 l with deionized water. 1 ml contains 0.6538 mg zinc.

EDTA solution. The $0.01M$ EDTA solution is prepared by dissolving approximately 3.723 g of disodium salt of ethylenediaminetetraacetic acid (EDTA) in deionized water and diluting up to 1 l. This solution is standardized against the standard copper solution and stored in polyethylene bottles.

Thiosulfate solution. The $0.025M$ thiosulfate solution is prepared by diluting a commercially available solution of thiosulfate (Acculute).

Buffer solution. Mix 162 ml of $1N$ acetic acid with 38 ml of $1N$ sodium acetate.

PAN indicator. 0.1% solution in methanol.

PROCEDURE

Preparation of automatic titrator. The "Spectro-Electro" titrator is switched to the "Spectro" position; the polarity switch thrown to position 1; the filter wheel turned to the 575 mμ position; the pegs in the base set to properly position the 50-ml beakers; the small stirrer, delivery tips, and burets connected; and the delivery set at about 3 ml/min for both titrants. The same conditions are suitable for both end-points, but in the case of the iodine titration a visible cut-off filter (Cobalt glass #5970, Corning Glass Co., Corning, N. Y.) is placed in the auxiliary filter holder in the titration compartment to allow only the transmission of the UV band at about 390 mμ.

Standardization of EDTA solution. Pipet a 5-ml aliquot of standard copper solution into a 50-ml beaker, dilute to about 25 ml with a 1:1 mixture of ethanol and water, adjust pH to about 4.0 with conc. ammonia (use pHydrion paper), add 2 ml of buffer solution and heat the solution to boiling. Add 3 drops of the PAN indicator and insert beaker in automatic "Spectro" titrator. Check that the visible cut-off filter is *not* in the light path and the titrant selector switch is in "EDTA" position; push the automatic start button to start stirring and delivery of titrant, and read the buret after automatic termination at the end-point.

Standardization of thiosulfate solution. Pipet a 10-ml aliquot of standard copper solution into a 50-ml beaker, dilute to approximately 25 ml with deionized water from which oxygen has been expelled by CO_2, adjust pH to approximately 4.0 with conc. ammonia, add 2 ml of buffer solution and 4–5 g of potassium iodide. Insert beaker in titrator, check that the visible cut-off filter *is* in the light path, the titrant selector switch is in "$Na_2S_2O_3$" position and the buret filled to the zero mark, turn on stirring and when the cuprous iodide is completely dissolved (about one min) and the solution clear, push the start button to start the delivery of thiosulfate solution and read the buret after automatic termination at the end-point.

Preparation of brass and bronze samples. Dissolve an accurately weighed sample of about 0.50 g of brass or bronze with 8 ml of 1:1 nitric acid in a 150-ml beaker. Heat gently and evaporate to about 3–4 ml. Dilute to approximately 80 ml with deionized water, heat nearly to boiling and adjust to pH 8–9 with conc. ammonia to precipitate sesquioxides of lead, manganese, and tin. Transfer the contents to 40-ml centrifuge tubes and centrifuge at about 2000 r.p.m. for 2–3 min. Transfer the supernatent liquid to a 500-ml volumetric flask, dissolve the precipitate with 1:1 HCl, reprecipitate with ammonia and centrifuge for one min. Transfer the supernatent liquid into the 500-ml flask and dilute up to volume with deionized water. This solution is used for both titrations.

Titration of copper. The same procedure as given for the standardization of thiosulfate solution is followed, except that the adjustment to about pH 4.0, prior to the addition of the buffer, is done with 1:3 HCl, because the solution is already ammoniacal.

Titration of total copper and zinc. Nearly the same procedure as given for the standardization of EDTA solution is followed even though zinc is also present. The only difference is that the adjustment to about pH 4.0, prior to the addition of the buffer, is done with 1:3 HCl, because the solution is already ammoniacal.

Zinc. Zinc is calculated by subtracting the volume of EDTA equivalent to the amount of copper found in the copper titration from the volume of EDTA used in the total Cu and Zn titration. A blank of 0.05 is also subtracted from the remaining volume.

CALCULATIONS

The percentages of copper and zinc can be rapidly calculated by equations (1) and (2), respectively, if the weighed sample is dissolved and made up to volume in a 500-ml volumetric flask, and a 10-ml aliquot taken for the titration of copper and a 5-ml aliquot taken for the titration of total copper and zinc.

$$\frac{A \times (B - 0.02) \times 5}{C} = D = \%\,\text{Cu} \quad \ldots\ldots\ldots\ldots \quad (1)$$

$$\frac{G \times (E - F - 0.05) \times 10}{C} = \%\,\text{Zn} \quad (2)$$

where,

A = mg of copper per ml of thiosulfate solution ($A = \frac{6.354}{H - 0.02}$, where H = ml of thiosulfate solution used in the standardization of thiosulfate solution).

B = ml of thiosulfate titrant used for the titration of copper in the sample.

C = weight of sample in grams.

E = ml of EDTA solution used in the titration of total copper and zinc.

F = ml of EDTA solution equivalent to the amount of copper found ($F = \frac{K - 0.05}{H - 0.02}(B - 0.02)$; where K = ml of EDTA solution used in the standardization of EDTA solution).

G = mg of zinc per ml of EDTA solution ($G = \frac{3.269}{K - 0.05}$).

RESULTS AND DISCUSSION

Analysis of solutions containing known concentrations of copper and zinc in different amounts and in different ratios gave the results shown in Table I. It is seen that the average absolute error is less than 0.003 mg for Cu, which is equivalent to about 0.002 ml of 0.025M thiosulfate solution, which is about the reading error of the 5-ml buret for the copper titration. The average absolute error is less than 0.007 mg for Zn, which is equivalent to about 0.01 ml of 0.01M EDTA solution, and this is approximately the reading error of the 10-ml buret used for the total copper and zinc titration.

TABLE I

AUTOMATIC TITRATION RESULTS FOR SAMPLES CONTAINING KNOWN AMOUNTS OF COPPER AND ZINC

Sample No.	Copper			Zinc		
	Taken, mg	*Found, mg*	*Difference*	*Taken, mg*	*Found, mg*	*Difference*
1	3.177	3.178	+0.001			
2	3.177	3.176	—0.001			
3	3.177	3.179	+0.002	1.961	1.956	—0.005
4	3.177	3.175	—0.002	1.961	1.960	—0.001
5	1.906	1.914	+0.008	1.961	1.953	—0.008
6	1.906	1.911	+0.005	1.961	1.947	—0.014
7	6.354	6.359	+0.005	0.654	0.664	+0.010
8	6.354	6.355	+0.001	0.654	0.660	+0.006
9	0.635	0.635	0.000	3.269	3.264	—0.005
10	0.635	0.633	—0.002	3.269	3.267	—0.002

Satisfactory results were obtained in the analysis of National Bureau of Standards brass and bronze samples (Table II). The average deviation is about 0.1% for both

TABLE II

AUTOMATIC TITRATION RESULTS FOR COPPER AND ZINC IN NBS BRASS AND BRONZE SAMPLES

NBS Number	*Cu %*			*Zn %*		
	Found	*Reported*	*Difference*	*Found*	*Reported*	*Difference*
Bronze 628	57.6			37.9		
	57.5			38.0		
	57.4			38.1		
	av. 57.5	57.39	+0.11	av. 38.0	37.97	+0.03
Silicon bronze 158	90.9			1.8		
	90.9			2.0		
	91.1			2.2		
	av. 91.0	90.86	+0.14	av. 2.0	2.07	—0.07
Bronze 164	63.5			21.1		
	63.3			21.4		
	63.2			21.3		
	av. 63.3	63.76	—0.46	av. 21.3	21.89	—0.59
Sheet bronze 37[a]	70.4	70.29	+0.11	27.1	26.89	+0.21
Cast bronze 52b[a]	88.5	88.25	+0.25	3.0	2.96	+0.04

[a] Average of triplicate results with the same precision as shown by the three other samples.

copper and zinc. The large negative errors for both Cu and Zn in NBS bronze sample #164 are due to its large content of interfering ions (6.21% Al, 2.52% Fe, 4.68% Mn) which results in a large coprecipitation of both copper and zinc during precipitation of the interfering ions. A double or even a third reprecipitation is recommended in samples very rich in interfering elements.

The delivery rate of the titrant was adjusted in the range of about 3 ml/min for the standardization of the EDTA solution and of the thiosulfate solution and all the titrations of copper and zinc samples. The adjustment of rate can be done with either a suitable capillary delivery tip or varying the opening of the teflon stopcock and pinch-off valve. At this delivery rate the titration time for total Cu and Zn is about 2 to 3 min for the analyzed samples, and the temperature of the solution at the end of the titration is about 55–65°. Under these conditions a blank of 0.05 ml of $0.01\,M$ EDTA solution is applied because of the small but reproducible overshooting of the equivalence point, and a blank of 0.02 ml is applied when thiosulfate is used as titrant.

The use of an excess of potassium iodide to dissolve the cuprous iodide, and stirring the solution before the start of the titration until it is clear are recommended in order to assure a large end-point signal sufficient to automatically terminate the titration. However, a turbid solution, due to incomplete solution of cuprous iodide can be used, but in this case an amplification of the small signal might be required to assure automatic termination at the end-point.

To minimize air oxidation of iodide during the titration of iodine, the solution is buffered at pH 4.0 and oxygen-free water is used for the dilution of the sample. The use of iodine as its own indicator simplifies the procedure[9]. At a pH of 4.0 sharp end-points were also assured in the titration of total Cu and Zn.

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An attempt was made to titrate Cu and Zn successively in the same aliquot sample. The solution was boiled after the titration of iodine with thiosulfate, and PAN indicator was added for the titration of zinc with EDTA. However, this reaction is quite sluggish and often the end-points were missed.

The thiosulfate solution can also be standardized against standard iodine solution (Acculute) or accurately weighed iodine. The EDTA solution was also standardized against standard $CaCO_3$ with Calcon as indicator, as previously reported[8]. The standardization methods against copper and $CaCO_3$ agreed within 0.2%.

Since the 0.5-gram samples were diluted to 500 ml and 5 and 10-ml aliquots taken for the EDTA and thiosulfate titrations, respectively, only 5 and 10 mg of actual sample were present for the two titrations.

ACKNOWLEDGEMENT

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SUMMARY

Direct automatic derivative spectrophotometric titration procedures for copper and zinc in brasses and bronzes are described. Copper reacts with excess iodide and the liberated iodine is automatically titrated with thiosulfate using the UV absorption band of iodine for end-point detection. Total copper and zinc is automatically titrated with EDTA using PAN as indicator, and zinc is found by difference. The automatic termination of the titrations eliminates the subjective evaluation of the end-points, and the entire procedure is simple, precise and accurate. The total time required for determining copper and zinc in brass or bronze is about twenty minutes.

RÉSUMÉ

Une méthode spectrophotométrique automatique rapide est proposée pour le dosage du cuivre et du zinc dans des laitons et des bronzes. Le cuivre est traité par un excès d'iodure; l'iode formé est titré automatiquement par spectrophotométrie au moyen de thiosulfate. La somme des teneurs en cuivre et zinc est ensuite déterminée automatiquement par titrage au moyen d'acide éthylènediaminotétracétique. La teneur en zinc est obtenue par différence.

ZUSAMMENFASSUNG

Es wird eine rasche automatische spektrophotometrische Methode zur Bestimmung von Kupfer und Zink in Messing und Bronzen beschrieben. Das Kupfer reagiert mit zugesetztem Jodid unter Bildung von freiem Jod, das mit Thiosulfat automatisch spektrophotometrisch titriert wird. Dann wird Kupfer + Zink durch automatische Titration mit EDTA bestimmt und der Zinkgehalt aus der Differenz errechnet.

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SPECTROPHOTOMETRIC DETERMINATION OF IRON WITH 2-HYDROXY-3-NAPTHOIC ACID

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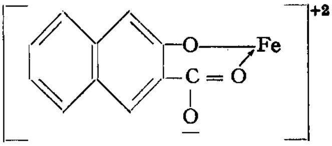
As early as 1834, the phenolic derivatives were tested[1] for their presence by their colour reaction with ferric ion, which subsequently was used for the detection of aromatic hydroxy derivatives. Salicylic acid[2] was the first of the aromatic hydroxy acids to be used for the quantitative determination of iron. Sulphosalicylic acid[3], salicyl aldoxime[4] and β-resorcylic acid[5] were other reagents used for the same purpose.

During our study of the phenolic derivatives[6,7] as colour-forming reagents, 2-hydroxy-3-napthoic acid has been found to behave as a very sensitive and highly selective reagent in its colour reaction with iron. The iron complex is soluble in water, but the excess reagent that is present along with the complex, comes out of solution. This, however, is prevented by the addition of gelatin, which as a peptising colloid stabilises and keeps the reagent as well as the complex in solution. The colour system so formed shows the maximum intensity of the colour at pH 2.9 to 3.1 with the maximum and minimum absorption regions, respectively, at 590 mμ and 420 mμ, within the range of 400 to 650 mμ. The sensitivity of the reaction is 0.25 μg/cm^2 (practical) and 0.025 μg/cm^2 (SANDELL). The system obeys Beer's law up to 24 p.p.m. of iron and the optimum range is from 4 to 20 p.p.m. of iron, where the per cent relative analysis error per 1% absolute photometric error is 2.9. The composition of the complex, as elucidated by the continuous variation, slope ratio and molar ratio methods, indicate that in solution the complex contains the metal and the reagent in the ratio of 1 : 1. The empirical formula of the complex may be suggested as: $[Fe(C_{11}H_7O_3)]^{+2}$ and may be represented structurally as:



The molar extinction coefficient of the complex is 2212 and the instability constant is about $4.29 \cdot 10^{-4}$.

Coloured ions or those ions that give coloured products are tolerated to a limited extent, while the complex-forming agents, like phosphate, fluoride, oxalate, citrate and tartrate, interfere with the determination of iron.

EXPERIMENTAL

Apparatus and solutions

The U.V. Spectrophotometer with 10.0-mm quartz transmission cells and the pH indicator were the same as used in a previous work[7].

Reagent solution

The reagent 2-hydroxy-3-napthoic acid of British Drug House, Ltd., was crystallised several times from alcohol till its melting point was between 222 and 223°. Because of its lower solubility in water, a 0.1% solution of the reagent in 95% ethyl alcohol was prepared and was used as the reagent solution throughout the work.

Iron solution

A standard solution of ferric nitrate was prepared from an Analar variety of the sample of British Drug House, Ltd. A weighed amount of the sample was dissolved in 100 ml water with the addition of 5 ml of nitric acid and was diluted to 1000 ml. The iron content of the solution, as determined gravimetrically, was found to be 1.727 mg/ml. Weaker solutions were prepared, as needed, by dilution.

Buffer solution

A sodium acetate-hydrochloric acid buffer of pH 3.0 was obtained by mixing normal solutions of sodium acetate (50 ml) and hydrochloric acid (48.5 ml) and diluting the solution with water to 250 ml.

Equimolecular solutions of ferric ion, the reagent for the study of the composition of the complex and a 0.2% (w/v) solution of gelatin were the other solutions prepared.

Other chemicals and solutions of diverse ions used were identical with those reported earlier[7].

Absorbance curves

An aliquot quantity of the iron solution was taken in a 25-ml volumetric flask and to it were added, in succession, 1 ml of the gelatin solution, 3 ml of the reagent solution, and 2 ml of the buffer to adjust its pH to 3.0. After dilution to 25 ml with water and thorough mixing, the absorption of the blue-coloured complex was measured against a reagent blank. Curves A and B in Fig. 1 show the maximum and minimum absorption regions of the colour system corresponding to 7.5 and 10.0 p.p.m. of ferric ions respectively; the regions in both cases are 590 mμ and 420mμ respectively, where the reagent has no absorption.

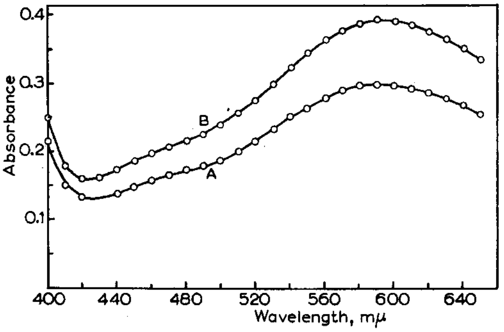


Fig. 1. Absorbance curves, A. 7.5 p.p.m. Fe; B. 10.0 p.p.m. Fe.

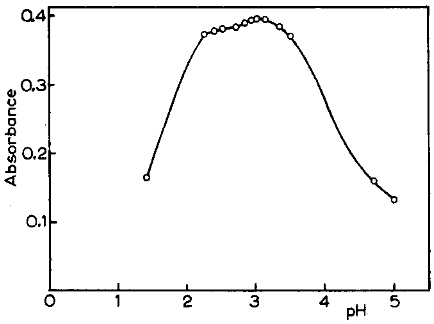


Fig. 2. Effect of pH; 10 p.p.m. Fe.

Effect of pH, reagent and time

The colour intensity is somewhat sensitive to changes in hydrogen concentration. Spectrophotometric measurements of a series of solutions with pH varying from 1.4 to 5.0 and always containing 10 p.p.m. of ferric ion, 1 ml of the gelatin solution and 3 ml of the reagent in a total volume of 25 ml, indicated that the colour intensity was at its maximum when the pH of the system was between 2.9 and 3.1. This restricted pH range necessitated the use of the buffer solution (2 ml) to adjust the pH of the system to 3.0. The optical density variation with pH is shown in Fig. 2.

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Similar studies of the effect of the reagent concentration on the colour system formed with 10 p.p.m. of ferric ion, 1 ml of the gelatin solution, 0.25 to 5.0 ml of the reagent solution and 2 ml of the buffer solution in a total volume of 25 ml were made and from the curve in Fig. 3 it appears that the maximum intensity of the colour is reached when the amount of reagent is only 2 ml of 0.1%, in a volume of 25 ml. For all subsequent measurements 3 ml of the reagent were always used.

The colour intensity of the iron–reagent complex changes with time, but for the first one hour the change is negligible as is evident from the curve in Fig. 3 and hence the optical density of the colour system was invariably measured immediately after preparation.

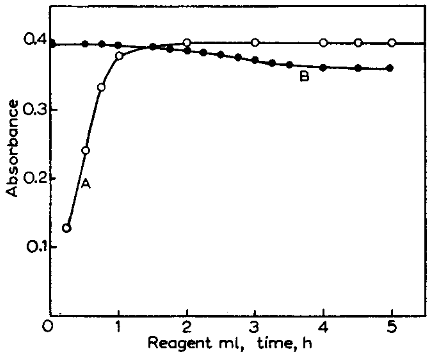


Fig. 3. A. Effect of reagent; B. Effect of time.

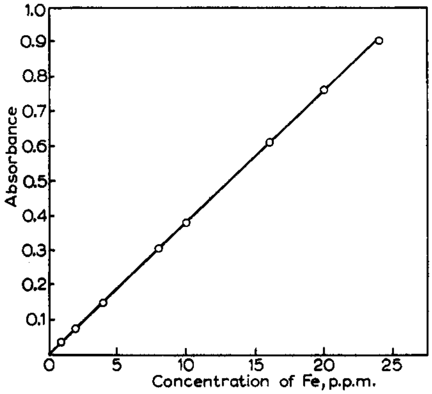


Fig. 4. Beer's law curve.

Beer's law, optimum range and photometric error

For the verification of Beer's law, optical densities at 590 mμ of a number of colour systems, with different quantities of ferric ion, measured against a water blank, were plotted against the respective concentrations of iron Fig. 4. Thus the systems were found to obey Beer's law with any iron concentration of 1 to 24 p.p.m.

Optimum range and accuracy in the photometric analysis of the proposed method were determined in the same way as described in the previous paper[7]. The optimum concentration range as obtained from the steep of the curve in Fig. 5 is from 4 to 20 p.p.m. of iron and the relative analysis error per 1% absolute photometric error for this range is 2.9%.

Effect of diverse ions

After the addition of the ion whose effect was to be studied, to the iron solution containing 10 p.p.m. of iron, the gelatin solution (1 ml), reagent solution (3 ml), and the buffer solution (2 ml) were added in the order stated. This was then diluted to 25 ml with water and its absorbancy was measured at 590 mμ. An ion was considered to interfere if the resulting solution differed by 0.005 in optical density (*cf.* Table I).

Such ions as phosphate, fluoride, oxalate, phthalate, citrate and tartrate which form complexes with ferric ion interfere. They either reduce the sensitivity or prevent the colour formation completely. Interference due to titanium was avoided by lowering the pH to 2.5.

TABLE I

Ion	*Added as*	*Limiting concentration p.p.m.*
Al^{+3}	$Al(NO_3)_3$	100
Ca^{+2}	$Ca(NO_3)_2$	100
Co^{+2}	$Co(NO_3)_2$	25
Cr^{+3}	$Cr(NO_3)_3$	30
Cu^{+2}	$Cu(NO_3)_2$	40
Cd^{+2}	$Cd(NO_3)_2$	100
Hg^{+2}	$HgCl_2$	30
Mg^{+2}	$MgCl_2$	60
Mn^{+2}	$MnCl_2$	40
Ni^{+2}	$Ni(NO_3)_2$	10
Th^{+4}	$Th(NO_3)_4$	50
Ti^{+4}	$Ti(SO_4)_2$	10
UO_2^{+2}	$UO_2(NO_3)_2$	20
Zn^{+2}	$Zn(NO_3)_2$	50
Zr^{+4}	$ZrOCl_2$	5

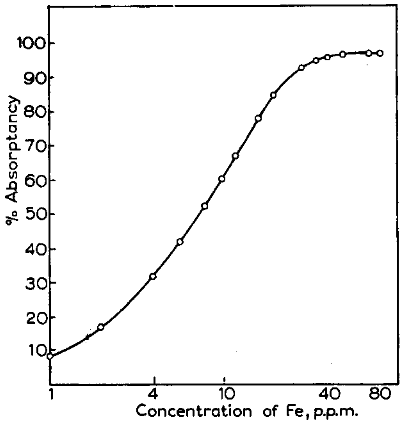


Fig. 5. Calibration curve for iron complex.

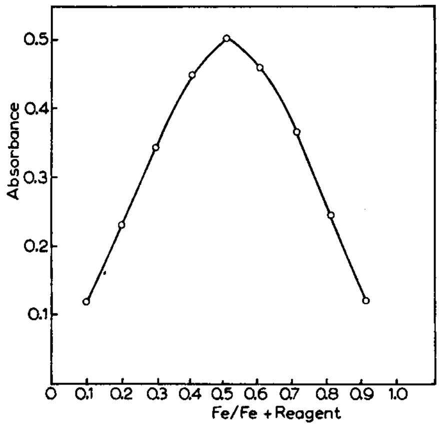


Fig. 6. JOB's method of composition.

Composition of the iron-2-hydroxy-3-napthoic acid

For the evaluation of the composition of the complex, the absorption of the mixtures (keeping the total volume constant) of equimolecular solutions ($1.33 \cdot 10^{-3}M$) of ferric ion and the reagent was measured at 590 mμ at which the iron and the reagent had no absorption. Fig. 6 is the true graphical representation of the absorption as plotted against the increasing amount of the ferric ion. The maximum indicates the formula of the complex to be $[Fe(C_{11}H_7O_3)]^{+2}$ where the iron and the reagent are in a ratio of 1 : 1.

Similar studies by the molar ratio method with equimolecular solutions ($5.32 \cdot 10^{-3}M$) of the ferric ion and the reagent yielded the identical composition of the complex.

Fig. 7, obtained with a fixed quantity of iron by plotting optical density against increasing amounts of the reagent, shows that the blue complex is formed when the ratio between the iron and the reagent is 1 : 1.

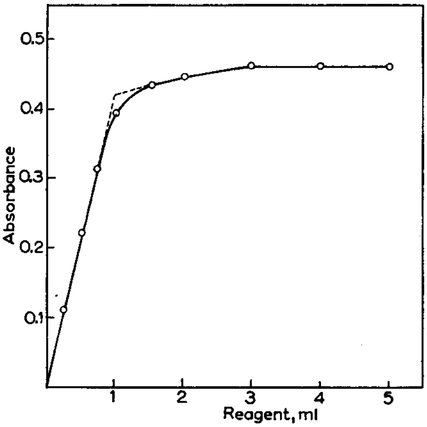


Fig.. 7. Molar ratio method.

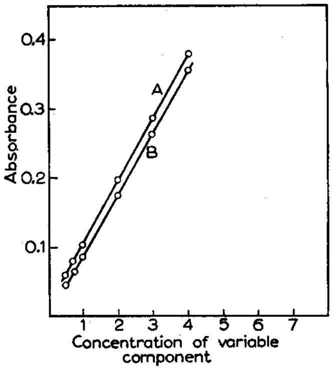
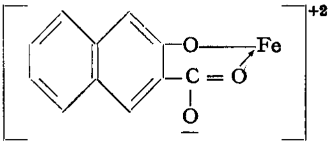


Fig. 8. Slope ratio method. A. reagent varying; B. Iron varying.

Confirmation of the above composition was provided by the slope ratio method and according to this, two series of solutions were prepared. In one series, the concentration of the reagent ($1.064 \cdot 10^{-3}M$) was varied in the presence of a constant excess of iron (5 ml of $5.32 \cdot 10^{-3}M$) and in the other, while the iron concentration ($1.064 \cdot 10^{-3}M$) was varied, the reagent was a constant component (5 ml of $5.32 \cdot 10^{-3}M$). The optical densities of the solutions were measured at the wavelength of the maximum absorption. The ratio of the slopes (Fig. 8) indicates a metal to reagent ratio of 1 : 1 in the complex.

In accordance with the views of WESP AND BORDE[8] regarding the complexes of ferric ion with phenolic derivatives and those of BENT AND FRENCH[9] and EDMONDS AND BIRNBAUM[10] for ferric thiocyanate complex, the composition of the soluble complex may be suggested to be $[Fe(C_{11}H_7O_3)]^{+2}$ while structurally it can be represented as



Extinction coefficient, degree of dissociation and instability constant

The molar extinction coefficient of the complex as calculated from Beer's law is 2212.

The degree of dissociation, α, has been calculated[11] from the relationship

$$\alpha = \frac{E_m - E_s}{E_m},$$

where E_m is the maximum absorption of a given amount of iron in the presence of

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a large excess of the reagent used to ensure the complete complexing of the iron and E_s is the absorption of the same amount of iron mixed with a stoichiometric quantity of the reagent. From absorption measurements at 590 mμ, where the reagent had no absorption, the E_m and E_s were found to be equal to 0.396 and 0.3390 respectively at an iron concentration of $1.791 \cdot 10^{-4} M$. Therefore, the degree of dissociation, α, was equal to 0.1432.

From the value of α, the instability constant, K, is obtained from the equation

$$K = \frac{\alpha^2 c}{1 - \alpha},$$

where c is the concentration of the complex in moles per l. Therefore,

$$K = \frac{1.791 \cdot 10^{-4} \cdot (0.1432)^2}{0.8568} \text{ or } K = 4.285 \cdot 10^{-4}$$

ACKNOWLEDGEMENTS

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SUMMARY

2-Hydroxy-3-napthoic acid is presented as a new, highly sensitive and selective reagent for its colour reaction with ferric ion. The sensitivity of the reaction is 0.025 μg/cm² (SANDELL). The blue-coloured complex is maximally absorbed at 590 mμ and obeys Beer's law up to 24 p.p.m. of iron. The optimum range of concentration is from 4 to 20 p.p.m. of iron, where the percent relative analysis error per 1% absolute photometric error is 2.9. The composition of the complex, as evaluated by JOB's method and as verified by the Molar and Slope ratio methods, shows that in solution, the complex contains the iron and the reagent in a ratio of 1 : 1. The empirical formula of the complex is suggested to be $[Fe(C_{11}H_7O_3)]^{+2}$. The molar extinction coefficient is 2212 and the instability constant of the complex is about $4.29 \cdot 10^{-4}$. Coloured ions or those ions that give coloured products are tolerated to a limited extent during the determination of iron.

RÉSUMÉ

L'acide hydroxy-2-naphtoïque-3 est proposé comme réactif sensible et sélectif pour le dosage du fer(III). La coloration bleue obtenue a une absorption maximum à 590 mμ et obéit à la loi de Beer pour des quantités de fer allant de 4 à 20 p.p.m. Les auteurs ont étudié également la constitution du composé formé.

ZUSAMMENFASSUNG

2-Hydroxy-3-naphtoesäure hat sich als ein empfindliches und selektives Reagens für die Bestimmung von Eisen-(III) erwiesen. Die erhaltene blaue Farbtönung besitzt ein Absorptionsmaximum bei 590 mμ; das Beer'sche Gesetz gilt für Konzentrationen von 4 bis 20 p.p.m. Es werden Angaben über die Struktur des erhaltenen Komplexes gemacht.

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SPECTROPHOTOMETRIC DETERMINATION OF COPPER WITH TIRON

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Sodium pyrocatechol disulphonate[1], disodium salt of 1,2-dihydroxybenzene-3,5-disulphonate, commercially known as Tiron, is a white crystalline compound highly soluble in water; its aqueous solution is stable for months. This reagent has been applied successfully for the colorimetric estimation of iron[2], titanium[3], molybdenum[4], cerium[5] and uranium[6].

In a neutral or alkaline medium, immediately on the addition of this reagent, copper forms a greenish-yellow complex and the sensitivity of its colour reaction is 2.5 p.p.m. of copper (0.24 $\mu g/cm^2$ according to SANDELL's definition) when measured at 375 mμ the region of maximum absorption. The complex adheres to Beer's law for a wide range of copper concentration, 10 to 160 p.p.m. of copper, and the ratio of metal to reagent in the complex as determined by Job's method[8] and confirmed by the method of molar ratio[2] is 1 : 2, with a dissociation constant on the order of $5.3 \cdot 10^{-6}$.

Ions of Fe^{+3}, Ti^{+4}, Ag^{+}, Au^{+3}, Nb^{+5}, Ta^{+5}, UO_2^{+2}, Ce^{+4}, MoO_4^{-2}, VO_3^{-}, CrO_4^{-2} and OsO_4 form coloured complexes and hence interfere in the determination of copper, but the ions of alkalis, alkaline and rare earths, Al^{+3}, Sn^{+4}, Zr^{+4}, Th^{+4}, Hg^{+2}, Pb^{+2} and WO_4^{-2} are tolerated when present in limited amounts.

EXPERIMENTAL

Apparatus and reagents

All absorption measurements were made with a U.V. Hilger's Spectrophotometer provided with a tungsten lamp, and quartz absorption cells of 1-cm light path. Corrections to compensate for the slight differences in the optical transmission of the cells were made whenever necessary.

pH measurements were made with a Cambridge pH indicator provided with an all-purpose glass electrode.

Standard copper solution

A standard solution of copper, containing 1 mg of copper per ml and having an acidity of 0.1*N* in sulphuric acid, was prepared from an A. R. variety of crystallised copper sulphate and its strength was determined gravimetrically by α-benzoinoxime.

Solutions of other ions were prepared from their reagent-grade salts and the amount of ion present per ml of each solution was estimated by standard procedure.

Solutions of sodium acetate (5*N*) and sodium hydroxide (1*N*) were prepared from their salts of analytical variety.

The reagent 'Tiron' was prepared according to COUSIN's[1] method and was crystallised several times from hot water. A 25-g portion of the reagent was dissolved in 500 ml distilled water in order to prepare a 5% solution of the reagent and solutions weaker than this were obtained by proper dilution.

Spectral transmittancy

For transmittancy measurements, a few ml of the copper solution were taken in a 25-ml flask and diluted with water to make up the volume, after the addition, in succession, of 5 ml each of the reagent and the sodium acetate solutions. After colour appeared, the solution was placed in the absorption cell and its transmittancy in different wavelengths was measured against a reagent blank containing 1% Tiron in 1*N* sodium acetate solution. Curves 1 and 2 in Fig. 1 show the absorption of the copper–Tiron complex corresponding to 80 p.p.m. of copper against the reagent and water blanks respectively, and curve 3 shows the absorption due to the reagent blank only. The maximum absorption region for the complex thus appears to be at 375 mμ.

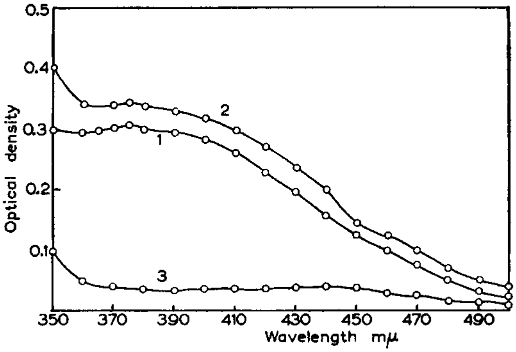

Fig. 1. Spectral transmittancy curves.

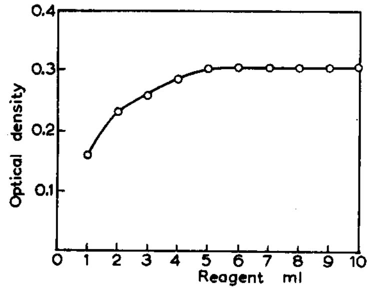

Fig. 2. Effect of reagent concentration.

Effect of reagent

Equal quantities of copper sulphate solution (80 p.p.m. of Cu) were taken separately in ten 25-ml flasks. Tiron solutions (5%) in different aliquots of 1 to 10 ml were added to each flask along with 5 ml of the sodium acetate solution. After making up the volume of each flask to 25 ml with distilled water, optical density of each solution was measured at 375 mμ against a water blank and each density measurement was corrected for the absorption due to the reagent. The curve in Fig. 2, representing the effect of the reagent, shows that when the reagent concentration is 1%, the intensity of the colour is maximal and remains so even with further amount of the reagent. Hence for subsequent work the concentration of the reagent was constantly maintained at 1%.

Effect of pH and time

At and above pH 8.0, the colour of the complex becomes deep yellow, and below pH 5.5, the full colour development does not take place. At a pH region of 6.1 to 6.9, the optical density was found to be always constant. Over pH 7.0, the shade changes with a shift of the maximum absorption to 430 mμ. Thus, for subsequent measurements the pH of the solution was kept at about 6.4 with sodium acetate.

The rate of reaction between copper and Tiron is instantaneous and the colour is stable for over 24 h. Though a negligible increase in intensity is observed in the first few hours, the intensity thereafter remains constant. Absorbancies, however, were measured immediately after mixing.

Beer's law

Copper sulphate solution taken in a 25-ml flask was treated in succession with 5 ml of the Tiron solution (5%), 5 ml of sodium acetate, and a few drops of the sodium hydroxide solution for the adjustment of pH. The solution was made up to 25 ml with water and its absorption was measured at 375 mμ against a reagent blank. On plotting the density against the concentration of copper (Fig. 3) it is observed that the system adheres to Beer's law within 10 to 160 p.p.m. of copper.

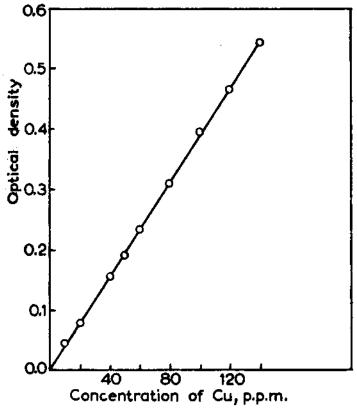

Fig. 3. Beer's law curve for copper–tiron complex.

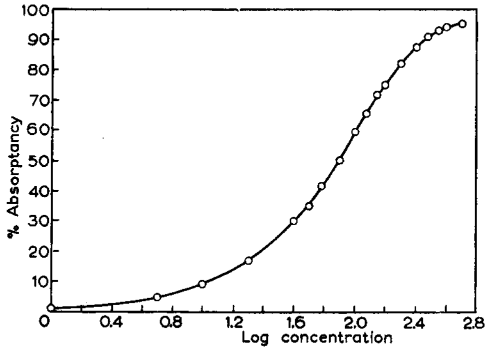

Fig. 4. Standard curve for copper–tiron complex.

Optimum range and accuracy

In order to define a suitable range and to evaluate the accuracy in photometric analysis, the percent absorbancy has been plotted as the ordinate against the logarithm of concentration as abscissa according to the proposal of RINGBOM[9]. It has been found that the optimum concentration range, as obtained from the slope of the curve (Fig. 4), is from 50 to 160 p.p.m. and for this range, the relative analysis error per 1% absolute photometric error as calculated from the equation[7] given below, is 2.94%.

$$\frac{\%\ \text{relative analysis error}}{1\%\ \text{absolute photometric error}} = \frac{230}{\mathrm{d}I/\mathrm{d}\log C}$$

Effect of diverse ions

The ions of Fe^{+3}, Ti^{+4}, Ce^{+4}, UO_2^{+2}, Nb^{+5}, Ta^{+5}, MoO_4^{-2}, CrO_4^{-2}, OsO_4, and VO_3^- yield colour reactions with the reagent. Au^{+3} and Ag^+ are reduced to the metallic state.

The ions of Ca^{+2}, Ba^{+2}, Sr^{+2}, Hg^{+2}, Pb^{+2}, Sn^{+2}, Sn^{+4}, Th^{+4}, Zr^{+4}, rare earths and WO_4^{-2} are found to form colourless complexes with no characteristic absorption in the visible region, though they consume some reagent and thus decrease the colour intensity of the copper–Tiron complex. Hence in the presence of a large excess of the reagent, these ions are tolerated to a limited extent.

For the study of the effect of the ions, copper sulphate solution (2 mg of copper) was taken in a flask along with the ion under investigation. 5 ml of the 5% reagent

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solution and 5 ml of the sodium acetate solution were added in succession, so as to adjust the pH to 6.4, and then water was added to make up the volume to 25 ml. The optical density of the solution was than measured against a reagent blank. An ion was considered to interfere if the resulting solution differed by 0.005 unit in optical density from that containing only copper and no diverse ions. Results are given in Table I.

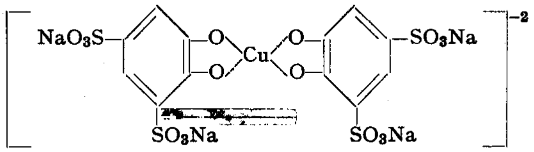
TABLE I

TOLERANCE TO DIVERSE IONS

Ion	*Added as*	*Limiting concentration p.p.m.*	*Ion*	*Added as*	*Limiting concentration p.p.m.*
Al^{+3}	$Al(NO_3)_3$	50	Mg^{+2}	$MgCl_2$	30
As^{+3}	$AsCl_3$	30	Mn^{+2}	$MnCl_2$	2
Be^{+2}	$BeCl_2$	5	Ni^{+2}	$Ni(NO_3)_2$	5
Bi^{+3}	$Bi(NO_3)_3$	6	Sb^{+3}	$SbCl_3$	10
BO_3^{-3}	H_3BO_3	10	Sn^{+2}	$SnCl_2$	5
Cd^{+2}	$Cd(NO_3)_2$	20	Sn^{+4}	$SnCl_4$	5
Co^{+2}	$Co(NO_3)_2$	4	Th^{+4}	$Th(NO_3)_4$	2
Hg^{+2}	$HgCl_2$	10	Zn^{+2}	$Zn(NO_3)_2$	15
			Zr^{+4}	$Zr(NO_3)_4$	5

Composition of the complex

The composition of the greenish-yellow soluble complex was studied by JOB's method[8] of continuous variation. Absorption due to mixtures (total volume kept constant) of equimolecular solutions at room temperature was measured at 375 mμ. The peak of the curve in Fig. 5, obtained by plotting the optical densities against increasing amounts of copper in complementary mixtures of copper and Tiron, indicates that the greenish-yellow complex has a composition in which the metal and the reagent are in a ratio of 1 : 2. The mole ratio method of YOE *et al.*[2] gives the same ratio (curves not shown). The reagent being a bidentate ligand, the complex may be represented as



Dissociation constant

From the absorption data of the mixtures of non-equimolecular solutions (Fig. 6), the dissociation constant K has been calculated according to the equation (see ref.[10])

$$K = \frac{C^{m+n-1} \cdot p^{(n-1)} \cdot [(pm + n)x - n]^{m+n}}{m^{n-1} \cdot n^{(m-1)} \cdot (p - 1)^{m+n-1} [n - (m+n)x]}$$

where m and n are 1 and 2 respectively, C is the molar concentration of copper, pc is the molar concentration of Tiron, x equals ml of the Tiron solution combining with the $(1-x)$ ml of the copper giving the maximum effect.

The instability constant K has been found by substituting the values of x, p and c in the above equation as given in Table II.

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TABLE II

Fig.	*Curve*	*Concn. of copper*	*Concn. of Tiron*	*x*	*p*	*K*
6	1	0.01M	0.02M	0.54	2	$2.15 \cdot 10^{-6}$
6	2	0.005M	0.02M	0.42	4	$8.4 . 10^{-6}$

Mean $K = 5.28 \cdot 10^{-6}$; the ionic strength is that of normal sodium acetate.

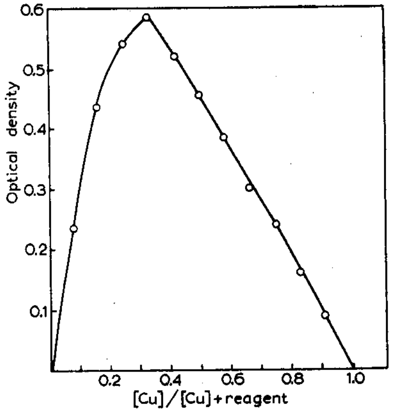

Fig. 5. JOB's method of continuous variation, $2 \cdot 10^{-2}M$ solutions.

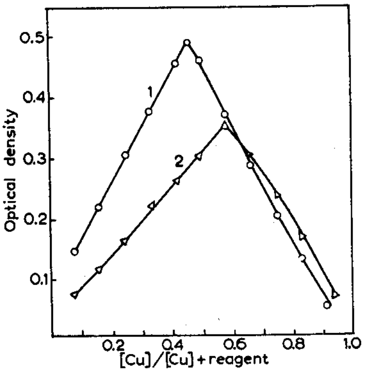

Fig. 6. Mixtures of non-equimolar solutions. (1) $2 \cdot 10^{-2}M$ reagent and $10^{-2}M$ Cu; (2) $2 \cdot 10^{-2}M$ reagent and $0.5 \cdot 10^{-2}M$ Cu.

SUMMARY

The reagent Tiron forms a soluble greenish-yellow complex with copper. The sensitivity of the colour reaction is 0.24 μg of copper/cm^2. The colour system at a pH of 6.1 to 6.9 is stable for over 24 h and shows a maximum absorption at 375 mμ. It obeys Beer's law at the latter wave length within a copper concentration of 10 to 160 p.p.m. The optimum range, however, is from 50 to 160 p.p.m. of copper, where the percent relative analysis error per 1% absolute photometric error is 2.94. JOB's method of continuous variation and the molar ratio method of YOE *et al.*[2] indicate that in solution the complex contains the metal and the reagent in a ratio of 1 : 2, with a dissociation constant on the order of $5.3 \cdot 10^{-6}$.

RÉSUMÉ

Le „tiron" est proposé comme réactif pour le dosage colorimétrique du cuivre. Il permet d'obtenir une coloration jaune verdâtre, stable, ayant une absorption maximum à 375 mμ.

ZUSAMMENFASSUNG

Zur colorimetrischen Bestimmung von Kupfer wird Tiron als Reagenz vorgeschlagen. Dieses bildet mit Kupfer einen stabilen, löslichen, grünlichgelb gefärbten Komplex, dessen Absorptionsmaximum bei 375 mμ liegt.

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THE DETERMINATION OF SMALL AMOUNTS OF TIN IN COPPER AND ITS ALLOYS

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INTRODUCTION

Until recently, analytical procedures for determining impurity amounts of tin in copper-base materials[1-12] have either been unsatisfactory or time consuming and the need existed for a simple rapid method, particularly for the examination of materials where specifications limit the tin content to 0.01%.

A qualitative test, in which phenylarsonic acid reacts with a solution of tin(IV) to produce a turbidity, has been published for the detection of 0.001% tin in analytical grade copper[13]. The 4-hydroxy-3-nitro derivative of this reagent was later used for determining tin in antimony sulphide[14] and, in 1956, this derivative was recommended for the determination of trace amounts of tin in refined copper[15], but no indication was given of the effect of impurities.

Over the past four years, these two reagents have been in regular use in our laboratories for the determination of tin in copper and copper alloys and, in view of the lack of published information on this subject, results of our experimental work are given in this contribution. The procedures described were developed for use with a Spekker absorptiometer because this instrument is in regular use in most control laboratories.

Part 1 of this paper describes the development of a turbidimetric procedure using phenylarsonic acid.

When iron is present above about 0.1%, an alternative procedure, using the 4-hydroxy-3-nitro derivative of phenylarsonic acid is necessary, and development of this procedure is described in Part 2.

PART 1 – USING PHENYLARSONIC ACID

Experimental

(*a*) *Preliminary tests*

It was established that a mixed hydrochloric–nitric acid solvent was preferable to the nitric acid (1 + 1) recommended for the qualitative test[13]. This mixed solvent enables higher amounts of tin to be determined because the resulting turbidity produced by the reagent is more finely dispersed whilst the limit of detection was about 0.001–0.002% on a 1-g sample. Transmission curves of solutions containing solvent, copper and tin were obtained using a Unicam spectrophotometer (S.P. 600). These tests indicated that an Ilford No. 601 filter was a convenient filter to use with a Spekker absorptiometer and all subsequent optical density measurements referred to in Part 1 were made with this instrument using a tungsten filament lamp, Ilford 601 filters and 1-cm cells.

(*b*) *Development of turbidity*

A tentative method was prepared and applied to 0.5-g samples of copper dissolved in 5 ml of a mixed hydrochloric–nitric acid solvent; varying amounts of a standard tin solution, covering the range 0.01 to 0.14% tin, were then added. The solutions were warmed to about 80° and to each was added 10 ml of an aqueous solution of phenylarsonic acid (5%). Each solution was cooled, the final volume was adjusted to 50 ml, and the optical density was determined after the turbidity had developed for 15, 30 and 60 min (Table I).

TABLE I

EFFECT OF STANDING TIME ON TURBIDITY

Tin added %	*Drum reading after:*		
	15 min	*30 min*	*60 min*
Nil	0.020	0.020	0.020
0.01	0.055	0.070	0.070
0.02	0.115	0.135	0.130
0.04	0.195	0.185	0.175
0.06	0.290	0.275	0.260
0.10	0.495	0.430	0.390
0.14	0.515	0.335[a]	0.335[a]

[a] Precipitate appeared

Although limited in number, these tests indicate that when the tin content does not exceed about 0.02%, a time interval of about 30 min is essential in order to ensure maximum development of the turbidity. Where tin up to 0.1% is present, it is essential to standardize the standing period and a time interval of 30 min was chosen as a convenient compromise. Based on this information a tentative procedure *(A)* was prepared and a calibration curve was constructed as detailed in the Appendix.

(*c*) *Effect of other elements*

Reagents containing the phenylarsonic group react preferentially with quadrivalent metals, particularly thorium, tin, titanium and zirconium[16]. Other metals, *e.g.* cerium(IV), hafnium, tungsten(VI) and uranium, yield insoluble compounds but none of these less common elements occurs in normal copper-base alloys. Iron(III), however, partly precipitates under these conditions and its effect, together with the effects of other metals likely to be encountered, was investigated.

Tests on a brass sample, reputed to contain 0.075% tin, indicated that zinc up to 40% and lead up to 2%, caused no interference. Further experiments were made in which iron and various other elements were added to a solution of the same brass sample; results of these tests are summarised in Table II.

Conclusions reached from the results shown in Table II are that, of the elements investigated, silicon and tellurium, in amounts normally present in copper-base materials, will only have a slight tendency to cause low results, but interference by iron is serious.

Attempts were made to overcome the effect of iron, and reagents such as citric, tartaric, phosphoric, hydrofluoric acid and/or ethylenediaminetetracetic acid were

TABLE II

EFFECT OF OTHER ELEMENTS

Element added:	—	Al[a]	Ni[a]	Mn[b]	Se[b]	Si[b]	Te[b]	Fe% 0.2	0.5	1.0	2.0	10.0
Tin (%) found:	0.075	0.071	0.071	0.076	0.074	0.060	0.064	0.064	0.018	0.009	0.009	0.002

Equivalent to [a] 10%, [b] 5%

all tried but none was entirely satisfactory. It was established by further experiments that, provided the iron and tin contents of the sample did not individually exceed about 0.06%, application of the tentative procedure is reliable. When tin exceeded 0.06%, lower sample weights were taken (see Appendix, *method A*, *Note 1*) and in this way, tin up to 0.4% could be determined with reasonable accuracy provided that the amount of iron present did not exceed the tin content of the sample.

Application of method to typical samples

Method A was applied to a selection of copper-base alloys and results obtained (Table III), are in reasonable agreement with results obtained by an alternative volumetric procedure based on a preliminary separation of tin as hydroxide, in the presence of added iron, reduction with hypophosphite and titration of the stannous solution with a standard potassium iodate–iodide solution[8,9].

TABLE III

RESULTS ON TYPICAL SAMPLES

Alloy	*Tin (%)* (*Turbidimetric procedure method A*)	*Volumetric procedure*
Brass 70/30 Cu/Zn	0.035 0.035	0.03
	0.035 0.035	0.03
	0.11 0.10	0.09
Leady brass (1.5% Pb)	0.33 0.30, 0.30	0.31
	0.26 0.23, 0.24	0.25
	0.15 0.14	0.14
	0.49 0.53	0.53
Leady brass (2.5% Pb)	0.20 0.22, 0.22	0.21
	0.29 0.28	0.28
	0.34 0.34	0.35
	0.46 0.48	0.44

The turbidimetric method is simple and rapid but the serious limitations imposed when iron is present, necessitated further experimental work and this is described in Part 2.

PART 2 – USING 4-HYDROXY-3-NITRO-PHENYLARSONIC ACID

Experimental

(*a*) *Preliminary tests*

Iron is an important constituent of several copper-base alloys, *e.g.* D.T.D. 197, specifies 4–6% iron, and limiting values for tin may be as low as 0.015%.

Because the 4-hydroxy-3-nitro derivative of phenylarsonic acid, subsequently referred to as 4H-3N-PA, is stated to offer advantages over the parent reagent, particularly in the presence of iron[14], use of this reagent was investigated. In the following experiments the final turbidity was developed in a dilute sulphuric acid solution because chlorides are known to interfere in the reaction[14].

Preliminary tests indicated that an acidity equivalent to about 2 ml of conc. sulphuric acid/50 ml was necessary in order to prevent precipitation of the ron–4H-3N-PA complex. Higher acidities were equally effective for this purpose, but formation of the tin–4H-3N-PA complex was delayed and a solution of minimum acidity was desirable. In the examination of copper-base samples a suitable acidity was obtained by dissolving 0.5 g of the sample in 10 ml of a nitric–sulphuric acid mixture; nitric acid was subsequently removed by evaporation. These experiments indicated that 4H-3N-PA was more sensitive than the parent phenylarsonic acid and tests on the limit of detection are detailed later.

Transmission–wavelength curves were prepared, using a Unicam spectrophotometer (S.P. 600), and it was shown that the reagent, in a sulphuric acid solution containing copper only, had negligible absorption over the wave-length range 4600–5000 Å; in the presence of tin, maximum absorption occurred at 4700 Å.

Using the tentative procedure (*B*) and a Spekker absorptiometer (tungsten filament lamp), Ilford 602 filter and 1-cm cells, a calibration graph covering the range 0.01–0.06% tin was prepared.

(*b*) *Effect of iron*

Initial experiments indicated that iron up to 0.25% had no significant effect on the determination. With higher amounts of iron, up to 1.5%, the standing period had to be increased from 30 to 90 min in order to obtain full development of the turbidity.

TABLE IV

EFFECT OF IRON

Total iron present %	*Tin (%) after standing for*		
	90 min	*3 h*	*20 h (Overnight)*
1.6	0.030	0.031	—
2.6	0.025	0.027	—
3.6	0.019	0.024	0.031
5.1	0.015	0.020	0.028
6.6	0.011	0.013	0.026

Further tests were made on solutions containing 0.5 g of a copper–nickel–iron alloy (0.03% tin and 1.6% iron) to which various additions of iron were made. Results obtained are summarised in Table IV.

These results indicate that maximum turbidity is obtained after about 3 h provided the iron content does not exceed about 2.0%. In the examination of samples containing iron in excess of this amount formation of the turbidity was incomplete and precipitation occurred. In subsequent tests, where iron exceeded 2.0%, the tin complex was allowed to settle overnight, it was then filtered, ignited, dissolved and examined for tin as in the absence of iron. Details of this modification are given in *Method C* and the results obtained on typical samples (Table V) are in reasonable agreement with those obtained by the volumetric method[8,9].

(*c*) *Effect of other elements*

Various additions were made to solutions containing 0.5 g of copper and the equivalent of 0.03% of tin and it was shown that the following elements had no significant effect in the determination.

TABLE V

RESULTS ON SAMPLES CONTAINING IRON, USING THE MODIFIED PROCEDURE

Iron present %	*Tin (%)*	
	Volumetric procedure	*Proposed procedure (method C)*
4–6	0.025	0.026
4–6	0.023	0.022
4–6	0.023	0.018
4–6	0.060	0.061
4–6	0.032	0.036
11.6	0.030	0.027
11.6	0.030	0.025
6.6	0.030	0.027

Aluminium (10%), antimony (0.10%), arsenic (10%), bismuth (1.0%), cadmium (10%), chromium (0.5%), lead (5%), nickel (10%), phosphorus (1%), selenium (5%), silicon (5%) and tellurium (1%).

Lead and silicon had no effect providing they were removed by filtration, after fuming with sulphuric acid. Antimony above 0.1% and up to 1% did not interfere, provided 1 g of tartaric acid was added before addition of the reagent. Reference has been made to the possible presence of tin oxide in copper[17] and although no evidence of oxide has been encountered, provision for this eventuality is made in the method.

(*d*) *Limit of detection*

Using 2 g of electrolytic copper and known additions of tin, it was found that the limit of detection of tin was about 0.0002%. The slight modification required for this increased weight is detailed in *Method D.*

Application of 4-hydroxy-3-nitro-phenylarsonic acid method

The proposed *Method B* was applied to 6 independent samples of copper–nickel–iron alloys, each containing about 1.5% iron and under 0.05% tin. Results (Table VI) obtained by two analysts, are in close agreement with those obtained by the volumetric procedure[8, 9].

TABLE VI

COMPARISON OF VOLUMETRIC AND TURBIDIMETRIC METHODS

Tin (%)			
Volumetric procedure	*Proposed procedure (method B)*		
	Analyst A	*Analyst B*	
0.020	0.018	0.019	0.020
0.024	0.025	0.027	0.027
0.020	0.017	0.019	0.019
0.020	0.018	0.021	0.020
0.029	0.031	0.033	0.033
0.039	0.037	0.037	0.039

Similar agreement between the two methods was obtained on two samples of brass containing about 2.5% of lead and about 0.4% of tin.

Further tests were made on a sample of brass (copper 58%, lead 3%, and iron 0.25%). Six determinations on aliquots from a stock solution gave results ranging between 0.275 and 0.290% tin. Four tests on independently weighed samples of the same material gave results of 0.285, 0.290. 0.270 and 0.275% tin compared with a single value of 0.29% obtained by the alternative volumetric procedure.

Method D, for application when tin is below 0.01%, was applied to nine samples of pure brass (copper 70%, zinc 30%) and results obtained (Table VII) were in good agreement with those obtained by the volumetric procedure.

TABLE VII

Sample	*Tin (%)*	
	Proposed procedure (method D)	*Volumetric procedure*
A	0.0015	0.001
B	0.0055	0.005
C	0.003	0.003
D	0.002	0.0015
E	0.0015	0.0015
F	0.0025	0.002
G	0.0035	0.004
H	0.003	0.003
I	0.006	0.0065

CONCLUSIONS

Compared with other known procedures for determining tin in copper-base materials, the proposed procedures are quicker, simpler and sufficiently accurate for determining tin up to about 0.4%.

Of the two recommended turbidimetric methods, the phenylarsonic acid method is the more rapid but it is less sensitive and, without modification, is limited in its application to samples containing under 0.1% iron. With this exception, usual impurities and alloying metals, normally associated with copper and its alloys, do not interfere. This method is, therefore, particularly useful for use in routine control laboratories.

The procedures, using 4H-3N-PA are more time consuming but are applicable in the presence of alloying amounts of iron and are recommended for the examination of typical copper-base materials.

The higher sensitivity of the 4H-3N-PA derivative offers distinct advantages for the determination of trace amounts of tin. On a 2-g sample, tin as low as 0.0002% can be detected and tin in excess of 0.001% can be determined accurately and rapidly. Fourteen samples containing 0.001–0.006% tin can be completed in about six hours, whereas other methods take considerably longer and are more difficult to apply, particularly in the examination of complex copper alloys containing appreciable amounts of iron, aluminium and manganese, *e.g.* D.T.D. 197 alloys.

The recommended procedures have now been in use in our routine laboratories for about four years and over this period a satisfactory order of reproducibility and accuracy has been maintained. Selectivity of the reagents and the relative simplicity of the methods suggest wider applications, provided metals which produce turbidities under similar conditions, *e.g.* titanium and zirconium, are absent.

ACKNOWLEDGEMENT

We thank Mr. W. T. Elwell for helpful suggestions in the preparation of this paper.

APPENDIX

METHODS FOR THE TURBIDIMETRIC DETERMINATION OF TIN IN COPPER ALLOYS

Method using phenylarsonic acid

Method A: For tin contents 0.01–0.4% (iron not exceeding 0.06%) – Note 1

Reagents

Nitric–hydrochloric acid mixture. To 50 ml of water add 32 ml of nitric acid ($d = 1.42$) and 12 ml of hydrochloric acid ($d = 1.18$). Cool and dilute to 100 ml.

Phenylarsonic acid solution (5%) Dissolve 5 g of phenylarsonic acid in warm water and dilute to 100 ml. This reagent must be freshly prepared and filtered before use.

Standard tin solution. Weigh the calculated amount of a bronze, of known tin content (about 10%), so that the sample contains 10.0 mg of tin. Dissolve in 5 ml of nitric–hydrochloric acid mixture and dilute to 100 ml. (1 ml contains 0.1 mg tin) This solution must be freshly prepared.

Preparation of calibration graph

Transfer 0.5 g of pure copper (tin free) to each of six 150-ml. beakers, add 5 ml of nitric–hydrochloric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 2.0, 3.0 and 4.0 ml of the standard tin solution (1 ml = 0.1 mg tin) to five of the copper solutions; use the remaining solution as a blank on the reagents.

Proceed with each as follows: Dilute to 30 ml, heat to boiling, remove from the source of heat and add immediately 10 ml of phenylarsonic acid solution (5%) (heated to 80°). Cool to 20° and dilute to 50 ml in a calibrated flask. Allow to stand for 30 min, shake the flask, then measure the optical density at a wavelength of 4200 Å. For measurements on a Spekker absorptiometer use a tungsten filament lamp, 1-cm cell and Ilford 601 filters.

Correct for the blank and prepare a calibration graph.

Procedure

Transfer 0.5 g of sample (*Note 1*) to a 150-ml beaker. As a blank on the reagents used, transfer a similar weight of copper (tin free) to a 150-ml beaker and proceed as for the examination of the sample. Add 5 ml of the nitric–hydrochloric acid mixture, and heat gently until the metal has dissolved. (*Note 2*). Adjust the volume of the

TABLE VIII

Sample weight g	*Tin content* %	*Maximum iron permissible* %
0.5	0.01–0.06	0.06
0.2	0.05–0.15	0.15
0.1	0.10–0.30	0.30
0.05	0.20–0.4	0.40

solution to about 30 ml and continue as described for the preparation of the calibration graph *(Note 3)*. Correct for the blank value and calculate the tin content of the sample by reference to the calibration graph.

Notes

1. If the tin content is above 0.05%, a lower sample weight must be used. The maximum permissible iron content is then increased (Table VIII).

2. If a residue is observed, filter the solution through a close texture filter-paper and wash with warm water. Calcine the paper and insoluble matter in a silica crucible and cool. Fuse the residue in 0.5 g of potassium bisulphate, cool, dissolve in 10 ml of hydrochloric acid (1 + 10), add the solution to the filtrate and proceed as recommended.

3. If the optical density exceeds 0.50, repeat the determination using a smaller sample weight. Excessive amounts of tin may lead to partial deposition of the complex and cause low results.

Methods using 4-hydroxy-3-nitro-phenylarsonic acid

Method B: For tin contents 0.01–0.4% tin (iron not exceeding 2.0%) – Note 1

Reagents

Nitric–sulphuric acid mixture. To 110 ml of water add 50 ml of nitric acid (d = 1.42) and 40 ml of sulphuric acid (d = 1.84).

4-Hydroxy-3-nitro-phenylarsonic acid reagent (4H-3N-PA) (2%). Dissolve 2 g of the reagent in 30 ml of methyl alcohol and dilute with water to 100 ml. This reagent must be freshly prepared and if necessary filtered before use.

Standard tin solution. As for *method A*.

Preparation of calibration graph

Transfer 0.5 g of pure copper (tin free) to each of seven 150-ml beakers, add 15 ml of nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 1.5, 2.0, 2.5 and 3.0 ml of the standard tin solution (1 ml = 0.1 mg tin) to six of the copper solutions, use the remaining solution as a blank on the reagents. Proceed with each solution as follows:

Evaporate until white fumes of sulphur trioxide appear, cool, wash down the side of beaker with 20 ml of water and heat until solution of salts is complete. Cool to 20°, add 10 ml of the 4H-3N-PA solution (2%) and dilute to 50 ml in a calibrated flask. Allow to stand for 30 min, shake the flask and then measure the optical density at a wavelength of 4700 Å. For measurements on a Spekker absorptiometer use a tungsten lamp, 1-cm cell and Ilford 602 filters.

Correct for the blank value and prepare a calibration graph.

Procedure

Transfer 0.5 g of sample to a 150-ml beaker *(Note 1)*. To provide a blank on the reagents used, transfer a similar weight of pure copper (tin free) to a 150-ml beaker and proceed as for examination of the sample. Add 15 ml of nitric–sulphuric acid mixture and heat gently until the metal has dissolved *(Note 2)*. Evaporate until white fumes of sulphur trioxide appear, cool, wash the side of the beaker and cover with 20 ml of water and heat gently until all salts have dissolved *(Note 3)*. Cool, add 10 ml of the 4H-3N-PA solution (2%) and then proceed as described for preparation of the calibration graph. *(Notes 4 and 5)*.

Correct for the blank value and calculate the tin content of the sample by reference to calibration graph.

Notes

1. This sample weight is recommended for tin contents 0.01 to 0.03%. For higher percentages of tin a smaller weight of sample must be taken and the amount of solvent reduced (see Table IX).

TABLE IX

Tin content %	*Sample weight* *ml*	*Solvent acid* *g*
0.01 –0.03	0.5	10
0.025–0.08	0.2	8
0.05 –0.16	0.1	7
0.10 –0.30	0.05	7
0.20 –0.40	0.03	7

Where a sample weight of less than 0.5 g is taken, a higher iron content can be tolerated *e.g.* 5% iron on the 0.2-g sample and 10% for the lower weights.

For accurate determinations of 0.01–0.03% tin, the maximum iron permissible is restricted to 2.0% but this limit can be extended to 2.5% for routine determinations.

2. See *method A, Note 2,* but on this occasion dissolve the cooled bisulphate melt in 10 ml of sulphuric acid (1 + 99) and add the extract to the filtrate.
3. If lead or silicon is present, allow the solution to cool, filter off lead sulphate and/or silica on a close texture filter paper and wash with sulphuric acid (1 + 99). Evaporate the filtrate to 30 ml and continue as described in the procedure.
4. In the presence of iron in excess of 0.25%, up to 1.5%, allow to stand for 90 min before determining the optical density. In the presence of 1.5–2.0% iron (up to 2.5% for routine tests) allow to stand for 3 h. If the iron content is unknown, the optical density must be determined after 30, 90 min and 3 h. If the value is still increasing after 3 h then *Method C* must be used. If the iron content does not exceed about 1.5%, the minimum limit for tin is about 0.005%.
5. See *Method A, Note 3,* page 65.

Method C: For tin contents 0.01–0.03% (iron above 2.0%), e.g. D.T.D. 197 alloy

Use *Method B* up to the addition of the 10 ml of 4H-3N-PA solution (2%) then mix and allow the solution to stand overnight. Filter the precipitate, which consists of the tin complex and a small portion of iron, on to a close texture filter paper and wash with water. Transfer paper and precipitate to a silica crucible and calcine. Fuse in 2 g of potassium bisulphate and cool. Extract with water and transfer to a 150-ml beaker. Add 2 ml of sulphuric acid (*d*-1.84) and heat gently. Cool, add 10 ml of the 4H-3N-PA (2%) solution and proceed as described for the preparation of the calibration graph (*Method B*).

Correct for the blank value and calculate the tin content by reference to the calibration graph.

Method D: For tin 0.001–0.01% in copper (maximum iron 0.05%)

Reagents. As *Method B*

Preparation of calibration graph

Transfer 2 g of pure copper (tin free) to each of six 150-ml beakers, add 20 ml of the nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Cool and add separately 0.5, 1.0, 1.5, 2.0 and 2.5 ml of the standard tin solution (1 ml = 0.10 mg tin) to five of the copper solutions; use the remaining solution as a blank. Proceed with each solution as described under *"Preparation of calibration graph"* (*Method B,* p. 65).

Procedure

Transfer 2 g of sample to a 150-ml beaker. As a blank on reagents transfer a similar weight of pure copper (tin free) to a 150-ml beaker and proceed as for the examination of the sample. Add 20 ml of the nitric–sulphuric acid mixture and heat gently until the metal has dissolved. Examine the solution for any insoluble residue *(Method B, Note 2)*. Evaporate the combined solutions until white fumes of sulphur trioxide appear, then proceed as described for preparation of the calibration graph.

Correct for the blank value and calculate the tin content of the sample by reference to the calibration graph.

SUMMARY

Turbidimetric procedures are recommended for the determination of tin, over the range 0.001–0.4%, in copper-base materials. Compared with other known methods, these procedures are simpler and invariably quicker. The procedure using phenylarsonic acid is applicable provided the amount of iron in the sample does not exceed the amount of tin to be determined. In the examination of samples containing alloying amounts of iron and small amounts of tin, the use of a more sensitive reagent 4-hydroxy-3-nitro-phenylarsonic acid, is recommended particularly for the determination of tin below 0.01%. With the exception of iron both procedures are relatively free from interference by common alloying elements.

RÉSUMÉ

Des procédés simples et rapides sont proposés pour le dosage turbidimétrique de l'étain, dans des alliages à base de cuivre, au moyen de l'acide phénylarsonique. Lors de faibles teneurs en étain (< 0.01%), on recommande l'emploi de l'acide hydroxy-4-nitro-3-phénylarsonique.

ZUSAMMENFASSUNG

Es werden einfache und rasche Methoden beschrieben zur turbidimetrischen Bestimmung von Zinn in Kupferlegierungen mit Hilfe von Phenylarsinsäure. Bei sehr kleinen Zinnmengen(< 0.01%) wird die Verwendung von 4-Hydroxy-3-nitrophenylarsinsäure empfohlen.

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NON-AQUEOUS DETERMINATION OF INORGANIC SALTS

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The procedures available for determination of salts in nonaqueous solutions are mostly limited to analysis of amine salts and to salts of the alkali and alkaline earth metals. Little information is available on nonaqueous titration of other inorganic salts, particularly salts of strong acids and strong bases.

KOLLING[1] reviewed the literature on methods proposed for volumetric analysis of inorganic compounds in nonaqueous solutions through early 1956.

There are a number of limitations to the analysis of salts by titration with perchloric acid. Many inorganic salts that would behave as bases in acetic acid are insoluble in this solvent, many salts form gelatinous precipitates during the titration, and it is not possible to differentiate the salt being analyzed from carbonate or hydroxide impurity. Several of these limitations also apply to those methods suggested for analysis of acidic salts by titration with alkali methoxides.

One technique commonly employed for determination of salts of organic bases and acids is to liberate the base with an excess of alkali or the acid with an appropriate mineral acid, extract with a nonaqueous solvent, and subsequently titrate the isolated base with perchloric acid, or the acid with alkali methoxide[2].

The extraction technique was modified to eliminate its laborious and time-consuming features, and its applicability for salt analysis was extended by combining acidification with a strong acid, a simple extraction, and a differentiating titration with tetrabutylammonium hydroxide.

PRINCIPLE OF METHOD

In a previous study[3], it was shown that strong monobasic acids can be titrated differentially in the presence of polybasic acids. This suggested that it should be possible to determine salts somewhat similarly — namely, acidify the salt with an excess of sulfuric acid and differentially titrate the liberated acid and the amount of sulfuric acid which was not required to react with the cationic portion of the test sample. The cation is precipitated as the sulfate by addition of a nonaqueous solvent. Thereafter, the determination is equivalent to the differentiating titration of the two acids, the liberated and added.

PROCEDURE

The apparatus and preparation of reagent have been described previously[4,5]. Accurately weigh 0.5 mequiv. of salt into a 100-ml volumetric flask. Dissolve the salt in 1 ml of water and 2 ml of $1N$ sulfuric acid. Add up to 3 additional ml of water if necessary to affect solution. Dilute to volume with either pyridine or acetone, stopper, and shake vigorously. Titrate a 50-ml aliquot of the supernatant of the dilution potentiometrically with 0.1*N* tetrabutylammonium hydroxide, and determine the end-points from a plot of the volume of titrant *versus* millivoltage. Substract the solvent blank from the final end-point.

Two or more inflections are obtained in the potentiometric curve. In some instances a separate inflection or inflections are obtained for the acid liberated from the salt; in others the acid or one of the acid equivalents may titrate with either the first or second equivalent of the residual sulfuric acid. The volume of titrant for the desired salt is ascertained by difference in all cases.

EXPERIMENTAL

Analysis of high purity salts

In order to prove the procedure analytically correct, samples of high purity sodium oxalate and sodium nitrate were analyzed. The salts were dissolved in water, excess sulfuric acid was added which yielded solutions containing oxalic acid, sulfuric acid and sodium sulfate, and nitric acid, sulfuric acid and sodium sulfate, respectively. Addition of a nonaqueous solvent precipitated the sodium sulfate, and the oxalic–sulfuric acid, and nitric–sulfuric acid mixtures were resolved by differentiating titrations on aliquots of the supernatant. Fig. 1 illustrates the potentiometric curves for these titrations. The oxalic-sulfuric acid titrations were performed in acetone, the nitric–sulfuric acid titrations in pyridine. In the oxalic–sulfuric acid potentiometric curve, the first and third inflections represent neutralization of the two sulfuric acid equivs., the second and fourth, the two oxalic acid equivs. On ten analyses of sodium oxalate, a mean value of 99.80% was realized with a standard deviation

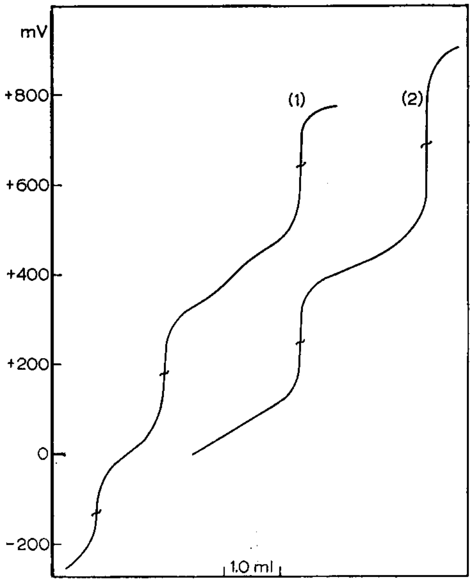

Fig. 1. Titration of sodium oxalate, (1), and sodium nitrate, (2), after acidification with sulfuric acid.

of 0.18. On ten analyses of sodium nitrate, a mean value of 99.60% was realized with a standard deviation of 0.31.

Analysis of representative salts

Table I lists a number of additional salts which were analyzed by this procedure. All salts were C.P. grade or better.

TABLE I

DETERMINATION OF SALTS BY ACIDIFICATION AND NONAQUEOUS TITRATION

Salt	*% Purity*	*Solvent*	*Number of inflections in potentiometric curve*
Sodium phosphate, dibasic ($Na_2HPO_4 \cdot 7H_2O$)	100.0 100.3	Acetone	3
Sodium phosphate, tribasic ($Na_3PO_4 \cdot 12H_2O$)	96.2 96.0	Pyridine	3
Sodium ammonium phosphate ($NaNH_4HPO_4 \cdot 4H_2O$)	99.5 98.9	Pyridine	3
Sodium phosphite ($Na_2HPO_3 \cdot 5H_2O$)	100.5 100.0	Acetone	5
Sodium chloride	97.2 97.3	Pyridine	2
Sodium bromide	99.4 99.2	Pyridine	2
Sodium nitrite	95.0 94.5	Pyridine	3
Potassium dichromate	99.0 98.5	Pyridine	2
Potassium chromate	97.2 97.3	Pyridine	2
Cupric acetate	100.1 100.9	Acetone	2
Nickel acetate	99.8 100.3	Acetone	2
Uranium acetate ($(UO_2)(C_2H_3O_2)_2 \cdot 2H_2O$	98.3 99.3	Pyridine	2
Potassium hydrogen phthalate	100.1 99.9	Pyridine Acetone	3 4
Sodium potassium tartrate ($NaKC_4H_4O_6 \cdot 4H_2O$)	99.0 99.5	Pyridine Acetone	3 3
Sodium citrate	99.0 98.9	Pyridine Acetone	4 4
Sodium perchlorate	97.2 97.5	Pyridine	2
Sodium chlorate	98.5 99.2	Pyridine	2
Uranyl zinc acetate ($(UO_2(C_2H_3O_2)_2 \cdot 2Zn(C_2H_3O_2)_2 \cdot 2H_2O$	99.1 99.5	Pyridine	2

The curves for some of the potentiometric titrations listed in Table I are shown in Figs. 2, 3, 4. The curve for sodium nitrate, sulfuric acid, illustrated in Fig. 1, typifies the titration of a strong monobasic acid and sulfuric acid; whereas, the curve for uranium acetate, sulfuric acid, illustrated in Fig. 2, typifies the titration of a weak

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monobasic acid and sulfuric acid. In the latter titration, the first inflection represents neutralization of the first equivalent of sulfuric acid, the second represents neutralization of the second sulfuric and the acetic equivalents. The curves for the phosphate salts with sulfuric acid are all similar to that given for trisodium phosphate, sulfuric acid in Fig. 2. In this curve, the first inflection represents neutralization of the sulfuric acid equivalent, the second represents neutralization of the second sulfuric acid and the first phosphoric acid equivalents, the third represents neutralization of the second phosphoric acid equivalent. The titration of sodium potassium tartrate, sulfuric acid in pyridine and of potassium hydrogen phthalate, sulfuric acid in acetone are illustrated in Fig. 3. In the first curve, the first inflection represents neutralization of the first sulfuric acid equivalent, the second, the first tartaric acid equivalent, the third represents neutralization of the second sulfuric acid and tartaric acid equivalents. In the second curve, the first and third inflections represent neutralization of the two sulfuric acid equivalents, the second and fourth, the two phthallic acid equivalents.

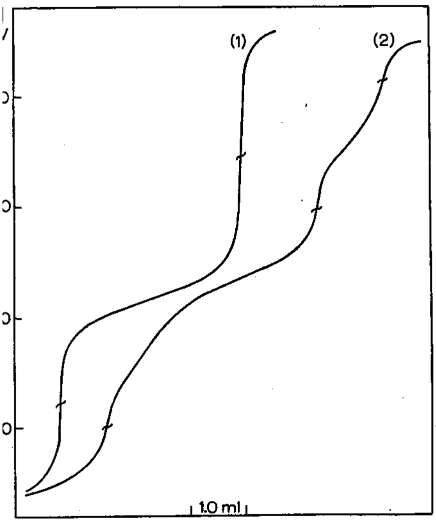

Fig. 2. Titration of uranium acetate, (1), and sodium phosphate, (2), after acidification with sulfuric acid.

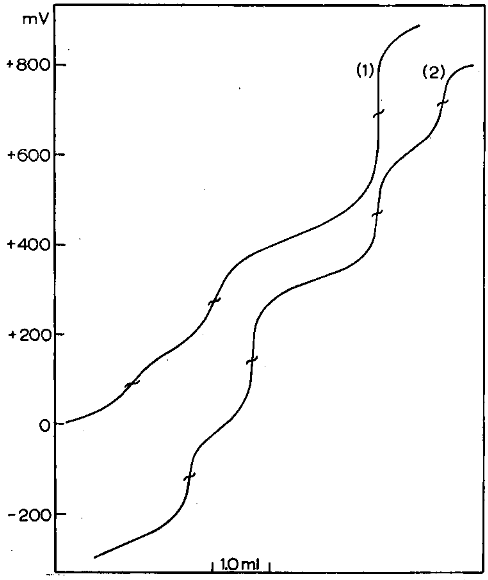

Fig. 3. Titration of sodium potassium tartrate, (1), and potassium hydrogen phthalate, (2), after acidification with sulfuric acid.

The titration of sodium phosphite, sulfuric acid, illustrated in Fig. 4, is of interest in that five inflections are discernible in the potentiometric curve. The first and fourth inflections represent neutralization of the two sulfuric acid equivalents, the volume of titrant from the first to the third end-point represents neutralization of the first phosphorous acid equivalent. The second end-point is equidistant from the first and third end-points and represents titration of one-half the phosphorous acid equivalent. The fifth inflection represents titration of the second phosphorous acid equivalent.

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Resolution of nitrate, nitrite mixtures

Nitrate, nitrite salt mixtures can be analyzed by this procedure. It was necessary in this analysis to hold the salt-acid reaction temperature below 5°. The titration of sodium nitrate and sodium nitrite mixtures after sulfuric acid acidification is illustrated in Fig. 5. The first inflection in the curve represents neutralization of the nitric acid and the first sulfuric acid equivalents, the second represents neutralization of the nitrous acid equivalent, and the third represents neutralization of the second sulfuric acid equivalent. The following calculations apply in determining the percent of each constituent in the mixture, titrating a 50-ml aliquot of the 100-ml dilution.

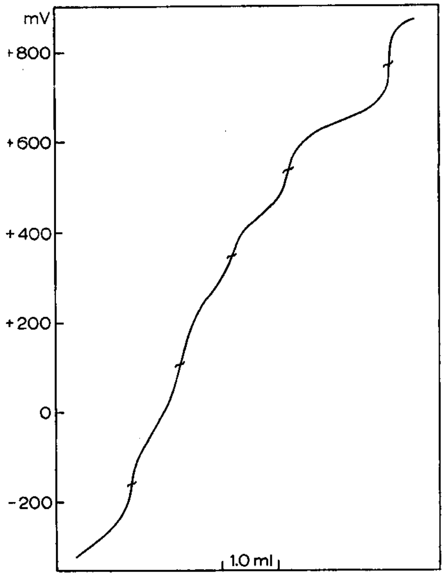

Fig. 4. Titration of sodium phosphite after acidification with sulfuric acid.

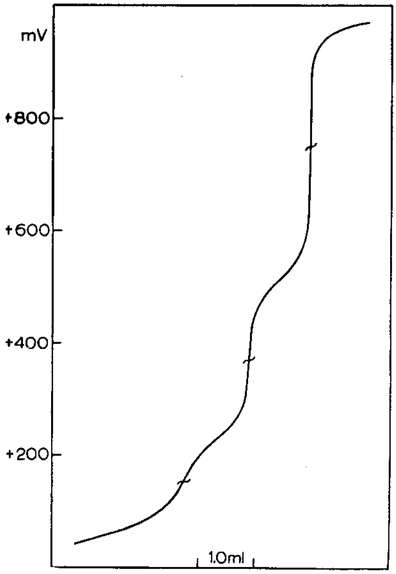

Fig. 5. Titration of sodium nitrite, sodium nitrate after acidification with sulfuric acid.

TABLE II

ANALYSIS OF SODIUM NITRATE—SODIUM NITRITE MIXTURES

Sodium nitrate			*Sodium nitrite*		
Added, mg	*Recovered, mg*	*% Recovery*	*Added, mg*	*Recovered, mg*	*% Recovery*
20.03	19.60	97.9	13.85	13.78	99.6
12.03	11.85	98.5	8.81	8.56	97.2
30.41	30.61	100.7	11.68	11.21	96.0
24.25	24.08	99.3	2.34	2.42	103.6
6.22	6.35	102.1	14.01	13.79	98.4

$$\%\ \text{Sodium nitrite} = \frac{2(V_2-V_1)(N.F.)(6.901)}{\text{Sample wt.}}$$

$$\%\ \text{Sodium nitrate} = \frac{2[V_1-(V_3-V_2)](N.F.)(8.501)}{\text{Sample wt.}}$$

where V_1 = volume of titrant to first end-point.
V_2 = volume of titrant to second end-point.
V_3 = volume of titrant to third end-point.
$N.F.$ = normality of tetrabutylammonium hydroxide solution.

Results from the analysis of known mixtures of sodium nitrate and sodium nitrite are listed in Table II.

DISCUSSION

In the proposed procedure, it is essential that the salt undergo an anion-exchange reaction with the acidifying agent, and that the two acids be resolved by a differentiating titration. These requirements would be fulfilled by a very wide variety of salts.

The carbonate and hydroxide impurities, if present, do not interfere in this procedure. It is possible to ascertain the carbonate or hydroxide impurity in a salt by adding an exact volume of standard sulfuric acid when acidifying. Any carbonate present reacts to form carbon dioxide, water, and the sulfate salt, the hydroxide to form water and the sulfate salt, none of which are titratable under the specified conditions. In the ensuing titration, the volume difference between the final end-point, and that for a blank sulfuric acid determination is a measure of the carbonate or hydroxide impurity.

Analysis of salts of strong acids and weak bases are not included in this study as they may be titrated directly with tetrabutylammonium hydroxide. These salts are dissolved in a minimum amount of water, the nonaqueous solvent added and the solution then titrated. Salts in this category, if water-insoluble, but acid-soluble, may be dissolved in a minimum amount of acid, and a differentiating titration performed after addition of a nonaqueous solvent.

SUMMARY

The procedures suggested for the determination of salts in nonaqueous solutions have been limited almost wholly to the analysis of amine salts and salts of the alkali and alkaline earth metals. Other salts are usually assayed by a variety of specific cationic or anionic procedures. By the proposed method, salts of all types can be determined titrimetrically so long as the compound will participate in an anion-exchange reaction. The procedure simply involves acidification of the salt with an excess of a strong acid, addition of a nonaqueous solvent and a differentiating potentiometric titration. Carbonate and hydroxide impurities do not interfere in the analysis and the solubility difficulties experienced in other nonaqueous procedures are not encountered in this method.

RÉSUMÉ

Une méthode titrimétrique est proposée pour le dosage des sels minéraux, en milieu non aqueux. Le procédé consiste à traiter le sel à analyser par un acide fort; on ajoute ensuite un solvant non aqueux et on effectue le titrage par potentiométrie.

ZUSAMMENFASSUNG

Es wird eine Titrationsmethode zur Bestimmung von mineralsauren Salzen in nicht-wässrigen Lösungsmitteln beschrieben. Das Salz wird mit einem Überschuss einer starken Säure und dem nicht-wässrigen Lösungsmittel versetzt und anschliessend potentiometrisch titriert.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

A. DOSAGE DE TRACES D'OR PAR LE VIOLET DE MÉTHYLE EN PRÉSENCE DE PLATINE

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Recherche du solvant

Les cations correspondants aux colorants basiques donnent avec certains anions des combinaisons extractibles par des solvants convenablement choisis. La recherche de la phase organique capable d'extraire aussi quantitativement que possible l'une de ces combinaisons est empirique car les connaissances actuelles sur les phénomènes de solvatation ne permettent pas de prévoir les solvants qui extraient une association donnée d'un anion et d'un cation. Toutefois l'expérience montre que seuls quelques solvants sont capables d'extraire les combinaisons d'un cation coloré donné. Précédemment, nous avons indiqué que les combinaisons de l'*o*-phénanthroline ferreuse étaient extractibles par le dichloro-1,2-éthane, l'alcool benzylique, l'*o*-nitrotoluène, l'*o*-bromotoluène. Le dichloro-1,2-éthane extrait quantitativement les combinaisons du bleu de méthylène avec les anions suivants: ClO_4^-, BF_4^-, IO_4^-, CNS^-, $Cl_3C{-}CO_2^-$, $AuCl_4^-$, $TlCl_4^-$. Les autres solvants chlorés: chloroforme, tétrachlorure de carbone, trichloréthylène; les hydrocarbures aromatiques et leurs dérivés halogénés, les cétones, esters, éthers, les plus courants ne dissolvent aucune de ces combinaisons.

On peut rechercher les solvants correspondant à un colorant donné, en utilisant l'une des combinaisons de ce colorant avec un anion en général facilement extractible comme CNS^- ou $Cl_3C{-}CO_2^-$. Il existe certainement des exceptions que cette méthode empirique ne permet pas de déceler, mais elle évite des essais fastidieux.

On trouvera quelques exemples dans le Tableau I:

TABLEAU I

Cations	*Solvants*
Violet de méthyle	trichloréthylène, toluène, *o*-bromotoluène, acétate de butyle, acétate d'isoamyle
Violet cristallisé	dipropylcétone (butyrone), méthylisobutylcétone (hexone)
Rouge neutre	cétones aromatiques, en particulier l'acétophénone
Safranine	acétophénone
Rhodamine B	benzène, acétate d'amyle, éther isopropylique

Les solvants utilisés doivent être très purs. En effet, la présence de traces d'acides organiques divers entraine souvent l'extraction du colorant en quantité telle, que

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tout dosage devient impossible. Les solvants chlorés en particulier doivent être redistillés, dans un appareil en verrerie rodée en l'absence de toute trace de corps gras. Cette purification est parfois insuffisante et doit être précédée d'un ou plusieurs lavages à l'aide de solutions alcalines.

Principe du dosage

Le complexe $AuCl_4^-$, comme ClO_4^-, IO_4^-, BF_4^-, $SbCl_4^-$, $TlCl_4^-$, $BiCl_4^-$, et plus généralement les anions du type LM_4^-, donne avec les cations de certains colorants basiques des combinaisons le plus souvent peu solubles dans l'eau, mais extractibles par une phase organique convenablement choisie. On a décrit par exemple, l'extraction du complexe $AuCl_4^-$ associé aux cations d'une benzylidène–rhodanine 1,2 (benzène, chloroforme) et de la rhodamine B[3] (éther isopropylique). Nous avons étudié l'extraction de ce complexe associé aux cations du bleu de méthylène (dichloro-1, 2-éthane) et du violet de méthyle (trichloréthylène). Ce dernier colorant a été finalement retenu pour la remarquable simplicité du mode opératoire. En effet, à un pH convenable, on peut extraire l'or et le séparer du platine dont le complexe $PtCl_6^{-2}$ n'est pas extractible. De même les ions Cl^- ne sont pas extraits; les nitrates gênent à partir d'une certaine concentration.

I. ÉTUDE DU DOSAGE DE L'OR

Réactifs utilisés

Solution de violet de méthyle. Solution aqueuse environ $10^{-3}M$ (0.4 g/l) du produit R.A.L. pour bactériologie.

Trichloréthylène. L'expérience montre qu'une simple distillation du produit ,,pur'' ou ,,technique'' est en général insuffisante pour éliminer certaines impuretés qui extraient d'importantes quantités de colorant. Le mode opératoire suivant a été adopté: après une première distillation, le solvant est placé dans une ampoule à décanter, et agité 2 fois pendant 5 min avec son demi-volume de soude normale, puis avec son volume d'eau distillée. Il est ensuite rectifié; on recueille la fraction passant à 87° ± 1°.

Solution d'or étalon. Une solution mère a été préparée par dissolution dans l'acide chlorhydrique normal d'environ 0.8 g de chlorure d'or par l. Le titre a été déterminé par gravimétrie (méthode à l'hydroquinone) et par volumétrie (iodométrie). La solution renfermait 0.360 g d'or par l. Elle a servi à préparer par dilution dans l'acide chlorhydrique $N/10$, une solution renfermant 5 µg d'or par ml.

Extraction de l'or

En désignant par HB^+ le cation coloré, la réaction d'extraction utilisée s'écrit:

$$\underset{\text{Eau}}{AuCl_4^- + HB^+} \rightleftharpoons \underset{\text{Trichloréthylène}}{(AuCl_4HB)_S}$$

A cet équilibre, correspond la relation

$$\frac{(AuCl_4^-)\ (HB^+)}{(AuCl_4HB)_S} = K$$

K étant fonction de la température.

Le coefficient de partage apparent est fonction de K et de (HB^+)

$$\frac{(AuCl_4HB)_S}{(AuCl_4^-)} = \frac{(HB^+)}{K}$$

L'expérience montre que la précision optimum des dosages de traces à l'aide des

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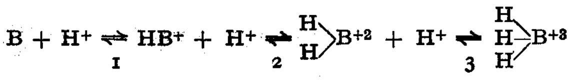
colorants est de l'ordre de 1 à 2%; on peut donc considérer l'extraction comme quantitative lorsque le coefficient de partage apparent est supérieur à 100. Si la constante K est très faible, le coefficient de partage peut rester supérieur à cette valeur lorsque la température et (HB^+) qui représente en première approximation la concentration du cation coloré dans la phase aqueuse, varient entre certaines limites. Mais le plus souvent, la valeur de K est telle que l'extraction n'est plus quantitative. On peut cependant effectuer un dosage, à condition de maintenir constant le rapport $(HB^+)/K$, en contrôlant la température et en maintenant constante la concentration du cation coloré. Cette concentration est fonction: (a) essentiellement du pH, (b) à un pH donné, de la quantité de colorant extrait. Or cette méthode ne s'appliquant qu'au dosage des traces, la concentration de la combinaison extraite dans la phase organique est toujours très faible (10^{-6} à 10^{-5} par exemple). Il suffit donc de choisir une concentration initiale du colorant en phase aqueuse telle que la fraction extraite soit négligeable ou de l'ordre de grandeur des erreurs d'expériences.

Influence du pH

Nous avons désigné le cation coloré par HB^+. Or de nombreux colorants basiques possèdent plusieurs fonctions amines auxquelles correspondent des cations de couleurs différentes. C'est le cas du violet de méthyle, colorant pentaméthylé du groupe du triphénylméthane qui présente vraisemblablement deux fonctions amines tertiaires et une fonction amine secondaire. Les cations correspondants à ces bases très faibles n'existent qu'en milieu très acide. On peut schématiquement représenter les trois systèmes acide-base par les équilibres:



$$B + H^+ \underset{1}{\rightleftharpoons} HB^+ + H^+ \underset{2}{\rightleftharpoons} \begin{matrix}H\\H\end{matrix}\!>B^{+2} + H^+ \underset{3}{\rightleftharpoons} \begin{matrix}H\\H\\H\end{matrix}\!>B^{+3}$$

Des nombreuses expériences que nous avons effectuées avec des colorants de ce type, il résulte en accord avec les travaux de D. E. RYAN[4] que c'est le plus souvent le cation monochargé HB^+ qui est extrait. Or, les pK des systèmes précédents sont très voisins; le cation extractible HB^+ qui participe aux équilibres 1 et 2 n'existe donc que dans un domaine de pH très restreint.

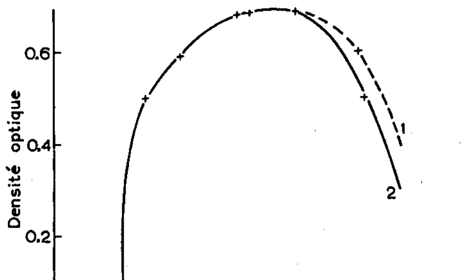


Fig. 1. Influence du pH sur l'extraction.

C'est dans ce domaine, correspondant à la concentration maximum du cation coloré HB$^+$, qu'il faut choisir le pH d'extraction afin d'obtenir le coefficient de partage apparent le plus élevé. Ceci n'est possible que si l'anion extractible existe à ce pH. Or, on sait que le complexe aurichlorhydrique AuCl$_4^-$ est très stable en milieu acide. Cependant en solution très diluée la stabilité de ce complexe peut-être fonction de la concentration des ions chlorures. Nous avons donc étudié l'extraction de cet anion en fonction du pH: (a) en maintenant constante la concentration des ions chlorures (1M) par mélange de solutions d'acide chlorhydrique et de chlorure de potassium entre pH 0.2 et pH = 2 (courbe 1, Fig. 1), (b) à l'aide de solutions d'acide chlorhydrique de titres variés entre HCl 4N et pH = 2 (courbe 2, Fig. 1).

Les autres facteurs de l'extraction sont maintenus constants: quantité d'or (18 μg), concentration du colorant dans la phase aqueuse ($2 \cdot 10^{-4}$), volume de la phase aqueuse (15 ml), volume de trichloréthylène (15 ml), température (20°), temps d'agitation (3 min).

Les deux courbes confondues entre pH = 0.2 et pH = 1.1 restent ensuite voisines, ce qui confirme la stabilité du complexe en milieu acide. On voit d'autre part que l'extraction est maximum entre pH = 0.8 et pH = 1.1; elle est d'ailleurs quantitative; une seconde extraction effectuée dans les mêmes conditions donne en effet une phase organique incolore.

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Maroc". Les spectres d'absorption de la molécule du colorant en milieu aqueux et de la combinaison extraite par le trichloréthylène sont représentés sur la Fig. 2.

La densité optique de la phase organique est mesurée au maximum d'absorption, soit pour $\lambda = 600.0$ mμ. La loi de Beer est suivie à ± 1% près (courbe 1 Fig. 3). Le coefficient d'extraction moléculaire à 20° est voisin de 115.000, ce qui permet de déceler avec une cuve de 2 cm une concentration limite de 10 à 15 μg d'or par l.

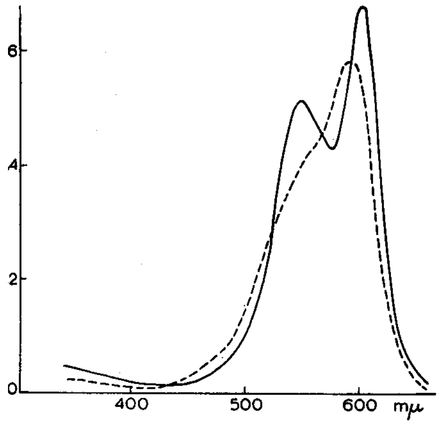


Fig. 2. Spectres d'absorption:
- - -: de la molecule de „Violet de Méthyle" en solution aqueuse (4 mg/l) —— : du complexe dans le trichloréthylène.

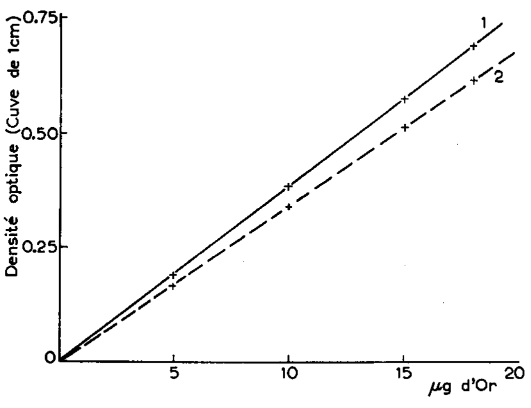


Fig. 3. Dosage de l'or: courbes d'étalonnage —— 1: à pH = 1 - - - - 2: en présence de platine à pH = 0.

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Cette méthode est plus sensible que celle décrite par MacNULTY et WOLLARD[3] qui préconisent l'emploi de la rhodamine B. En effet, le coefficient d'extinction moléculaire calculé à partir des résultats publiés par ces auteurs est voisin de 72.000.

Mode opératoire pour le dosage des traces d'or

Il est facile de déduire des résultats précédents, un mode opératoire s'appliquant au dosage de l'or en l'absence d'autres éléments, en particulier d'autres métaux précieux. Par exemple, pour 10 ml d'une solution dont le pH est voisin de 1: A 10 ml de la solution, ajouter 3 ml de la solution du colorant, 3 ml d'acide chlorhydrique 2 $N/10$, 15 ml de solvant. Agiter énergiquement trois minutes dans une ampoule à décanter non graissée. Après décantation, mesurer la densité optique de la phase organique à $\lambda = 600.0$ mμ. Un essai à blanc effectué dans les mêmes conditions en remplaçant la solution à doser par de l'acide chlorhydrique $N/10$, doit donner une phase organique incolore (la densité optique est généralement inférieure à 0.01). L'étalonnage est fait dans les mêmes conditions à l'aide d'une solution d'or de titre connu, renfermant par exemple 5 μg d'or par ml. Les nitrates gênent si leur concentration est supérieure à 10^{-4}.

II. DOSAGE DES TRACES D'OR EN PRÉSENCE DE PLATINE

Le complexe platichlorhydrique $PtCl_6^{-2}$ donne avec le cation monochargé du violet de méthyle un précipité:

$$PtCl_6(HB)_2 \underset{2}{\overset{1}{\rightleftharpoons}} PtCl_6^{-2} + 2\ HB^+$$

Ce composé peu soluble n'est pas extractible par le trichloréthylène et n'existe que dans le domaine de pH très restreint où se trouve le cation HB^+. Par exemple, avec une concentration du platine égale à $2 \cdot 10^{-3} M$ (0.4 g/l), et une concentration totale du colorant égale à $2 \cdot 10^{-4}$, le précipité n'existe qu'entre pH $= 0.3$ et pH $= 2.3$.

En présence de ce précipité, un dosage précis de traces d'or n'est plus possible: (a) la concentration du cation coloré devient très faible; elle dépend de l'équilibre précédent. L'extraction n'est plus quantitative, son rendement devient voisin de 60%. (b) La loi de Beer n'est plus suivie, les résultats ne sont pas reproductibles en particulier avec les quantités d'or inférieures à 10 μg.

Pour doser les traces d'or en présence de platine, il est donc nécessaire d'éviter la formation du précipité. Le plus simple est d'effectuer l'extraction à un pH convenable par exemple en milieu acide chlorhydrique normal. Dans ces conditions, l'extraction n'est plus quantitative (Fig. 1), mais le pH étant constant, la température contrôlée (20° ± 1° par exemple) et la concentration du colorant suffisante ($2 \cdot 10^{-4}$), la loi de Beer est suivie (courbe 2, Fig. 3).

Le mode opératoire est donc identique au précédent: il suffit de remplacer les solutions d'acide chlorhydrique $N/10$ par des solutions N. Les résultats sont reproductibles à 2% près environ.

En milieu acide chlorhydrique N, les nitrates ne gênent que si leur concentration est supérieure à $5 \cdot 10^{-2}$.

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RÉSUMÉ

Le complexe aurichlorhydrique $AuCl_4^-$, associé au cation du violet de méthyle, est extractible quantitativement vers pH = 1 par le trichloréthylène. Le coefficient d'extinction moléculaire est voisin de 115.000. A pH = 1, le complexe platichlorhydrique donne avec le colorant un composé peu soluble non extractible. En présence de ce précipité un dosage précis de l'or devient impossible; on peut éviter sa formation en effectuant le dosage vers pH = 0; la sensibilité diminue car l'extraction n'est plus quantitative.

SUMMARY

A description is given of the determination of traces of gold in solutions, either alone or in the presence of platinum, according to the extraction method, using methyl violet as complexing agent.

ZUSAMMENFASSUNG

Es wird die Bestimmung von Spuren-Mengen Gold in reiner Lösung sowie neben Platin mit Hilfe von Methylviolett nach dem Extraktionsverfahren beschrieben.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

B. DOSAGE DE TRACES D'ÉTAIN PAR LE VIOLET CRISTALLISÉ

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PRINCIPE

Nous avons pensé que l'utilisation d'un colorant basique permettrait la mise au point d'une méthode aussi fidèle mais plus sensible que celles récemment proposées utilisant des réactifs nouveaux, comme par exemple les dérivés de la fluorone[1-3]. Nous avons recherché une combinaison extractible d'un complexe négativement chargé de Sn(II) ou Sn(IV) avec le cation d'un colorant basique. C'est finalement le complexe chlorhydrique de Sn(II) ($SnCl_4^{-2}$ ou $SnCl_3^-$) associé au violet cristallisé qui a été retenu. Le solvant utilisé est la 4-heptanone (butyrone ou dipropylcétone). L'hexone (méthylisobutylcétone) peut être également employée, mais la sensibilité du dosage diminue.

La principale difficulté rencontrée au cours de cette étude a été la réduction des traces d'étain stannique en étain stanneux. Une méthode simple utilisant les propriétés réductrices de Ti(III) en présence de cupferron a permis de résoudre ce problème.

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Réduction des traces d'étain stannique

En solution, l'étain se présente le plus souvent à l'état stannique. Pour que la méthode proposée soit utilisable, il est donc nécessaire de réduire les traces d'étain(IV) aussi rapidement et aussi quantitativement que possible, par une méthode compatible avec les exigences de l'extraction: température, pH, concentration des différents ions reproductibles dans les différents essais. Les méthodes classiques utilisant les métaux réducteurs à l'état pulvérulent comme le fer ou le zinc s'adaptent difficilement à la réduction des traces et ne respectent pas ces conditions: les résultats ne sont pas reproductibles. L'emploi de cations très réducteurs comme V^{+2} ou Cr^{+2} s'est révélé inefficace.

On sait que la réaction: $\mathrm{Sn(IV)} + 2\ \mathrm{Ti(III)} \rightarrow \mathrm{Sn(II)} + 2\ \mathrm{Ti(IV)}$ est lente et incomplète. Or, en présence de cupferron, elle devient rapide et pratiquement quantitative. On peut ainsi réaliser rapidement la réduction des traces d'étain stannique dans le récipient d'extraction en présence d'un excès de réducteur et obtenir des résultats reproductibles; les ions du titane ne gênent pas pour la suite du dosage.

ÉTUDE DES DIFFÉRENTS FACTEURS

Réactifs utilisés

Solution étalon d'étain. Une masse connue d'étain pur (1 g environ) est attaquée par le minimum d'acide chlorhydrique concentré; on complète ensuite à 500 ml avec de l'acide chlorhydrique normal. On prépare ensuite une solution renfermant 2 µg d'étain par ml, par dilution avec de l'acide chlorhydrique normal.

Solution de cupferron. A préparer au moment de l'utilisation: 1 g du produit „Prolabo R.P." dans 50 ml d'eau.

Solution de chlorure titaneux. 35 g de la solution commerciale à 15% „Prolabo" dans 150 ml d'acide chlorhydrique normal. Cette solution-mère est conservée en atmosphère d'azote. Pour le dosage, on prépare au moment de l'utilisation une solution diluée 5 fois par de l'acide chlorhydrique normal.

Solution de violet cristallisé. Solution aqueuse à 3 g/l du produit R.A.L. pour bactériologie. La solution est agitée 1/2 h puis filtrée sur creuset de verre fritté No. 2.

Solvant. La 4-heptanone (dipropylcétone, butyrone) pure du commerce est agitée dans une ampoule à décanter avec deux fois son demi-volume d'hydroxyde de sodium normal, puis avec son volume d'eau distillée. Elle est ensuite rectifiée dans un appareil en verrerie rodée, non graissée. On recueille la fraction distillant entre 141 et 144°.

Étude qualitative de l'extraction

L'expérience montre que l'extraction par la butyrone de la combinaison du complexe chlorhydrique de Sn(II) et du violet cristallisé est accompagnée de l'extraction du chlorhydrate de ce colorant. Les deux réactions sont:

$$\text{I : } \underset{\text{Eau}}{\mathrm{SnCl_4^{-2}} + 2\ \mathrm{HB^+}} \underset{2}{\overset{1}{\rightleftharpoons}} \underset{\text{Butyrone}}{(\mathrm{SnCl_4H_2B_2})_s}$$

$$\text{avec } \frac{(\mathrm{SnCl_4^{-2}})\ (\mathrm{HB^+})^2}{(\mathrm{SnCl_4H_2B_2})_s} = K_1 \qquad (1)$$

$$\text{II : } \underset{\text{Eau}}{\mathrm{Cl^-} + \mathrm{HB^+}} \underset{2}{\overset{1}{\rightleftharpoons}} \underset{\text{Butyrone}}{(\mathrm{ClHB})_s}$$

$$\text{avec } \frac{(\mathrm{Cl^-})\ (\mathrm{HB^+})}{(\mathrm{ClHB})_s} = K_2 \qquad (2)$$

Le coefficient de partage apparent de l'extraction I peut s'écrire:

$$\frac{(\mathrm{SnCl_4H_2B_2})_s}{(\mathrm{SnCl_4^{-2}})} = \frac{(\mathrm{HB^+})^2}{K_1} = \frac{K_2^2}{K_1}\ \frac{(\mathrm{ClHB})_s^2}{(\mathrm{Cl^-})^2}$$

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Pour que ce coefficient de partage soit constant, il est donc nécessaire: d'effectuer l'extraction à température constante (K et K' sont fonctions de la température), de maintenir constante la concentration des chlorures en phase aqueuse et celle du chlorhydrate en phase organique. La relation (2) montre que cette dernière condition sera réalisée si pour une concentration donnée des chlorures, (HB^+) qui représente en première approximation la concentration du cation coloré à l'équilibre est constant. Nous avons montré dans le mémoire précédent que la concentration du cation coloré est pratiquement constante, si l'extraction est effectuée à pH constant, en présence d'une concentration du colorant telle que la partie extraite est négligeable devant la quantité totale.

Le dosage des traces d'étain à l'aide du violet cristallisé est donc possible malgré l'extraction simultanée de chlorhydrate du colorant à condition que les facteurs suivants soient maintenus constants: température, pH, concentration des chlorures et du colorant en phase aqueuse.

On sait que le complexe $SnCl_4^{-2}$ n'est stable qu'en milieu acide chlorhydrique, a pH < 1. L'extraction de ce complexe s'effectue donc en présence d'une forte concentration d'ions Cl^-, et bien que le coefficient de partage de l'extraction II soit certainement très faible, la phase organique obtenue est fortement colorée, par la présence du chlorhydrate de violet cristallisé (la densité optique est voisine de 5). Un dosage spectrophotométrique direct est donc impossible. Pour éliminer la plus grande partie du chlorhydrate, il est nécessaire d'effectuer un lavage de la phase organique en l'agitant un certain temps avec un volume donné d'une solution aqueuse convenablement choisie. Cette opération a pour but de déplacer l'équilibre de la réaction II dans le sens 2, en limitant autant que possible le déplacement de celui de la réaction I dans le même sens. En particulier, la solution de lavage doit être choisie de telle manière que le complexe $SnCl_4^{-2}$ y soit stable, afin d'éviter des réactions qui déplaceraient l'équilibre, telles que:

$$\text{III: } SnCl_4^{-2} \rightleftharpoons SnCl_3^- + Cl^-$$

$$\text{IV: } SnCl_3^- + H_2O \rightleftharpoons SnOH^+ + H^+ + 3\ Cl^-$$

C'est dire que cette solution doit être une solution d'acide chlorhydrique ce qui est incompatible avec le déplacement total de l'équilibre II dans le sens 2. Afin de trouver les conditions optima nous avons étudié systématiquement le lavage de la phase organique par des solutions d'acide chlorhydrique de concentrations variées.

Lavage de la phase organique

Les résultats sont représentés par les courbes de la Fig. 1: la densité optique de la phase organique est portée en ordonnées, le titre en acide chlorhydrique de la phase aqueuse de lavage en abscisses.

La courbe 1 représente la densité optique de la butyrone, renfermant un mélange de chlorhydrate $(ClHB)_S$ et de la combinaison $(SnCl_4H_2B_2)_S$ après lavage par des solutions d'acide chlorhydrique de concentrations diverses.

La courbe 2 représente la densité optique de la butyrone ne renfermant que le chlorhydrate, après lavage par les mêmes solutions. Le volume de la phase aqueuse est le double de celui de la phase organique. Ces phases organiques sont obtenues par extraction dans des conditions opératoires décrites plus loin, la première d'une solution chlorhydrique renfermant une quantité connue d'étain (6 μg) la seconde d'une solution chlorhydrique identique ne renfermant pas d'étain; c'est ce que nous appelons ,,l'essai à blanc''. La courbe 3 est la différence des courbes 1 et 2. Elle représente la densité optique de la combinaison ($SnCl_4H_2B_2$) seule; elle permet donc de déceler la concentration optimum de la solution chlorhydrique de lavage: 0.65N. C'est pour cette concentration que le déplacement de l'équilibre I dans le sens 2 est minimum, alors que le déplacement de l'équilibre II dans le sens 2 permet d'obtenir une densité optique de l'essai à blanc voisine de 0.30 (courbe 2), valeur suffisamment faible pour que des mesures spectrophotométriques précises soient possibles.

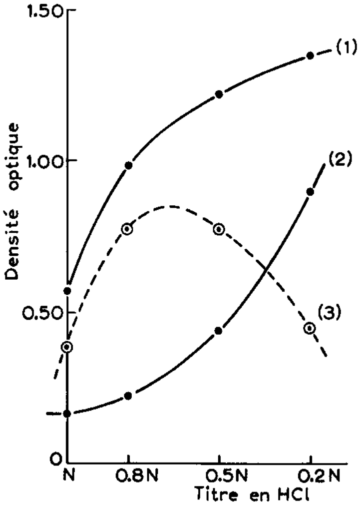

Fig. 1. Lavage de la phase organique.

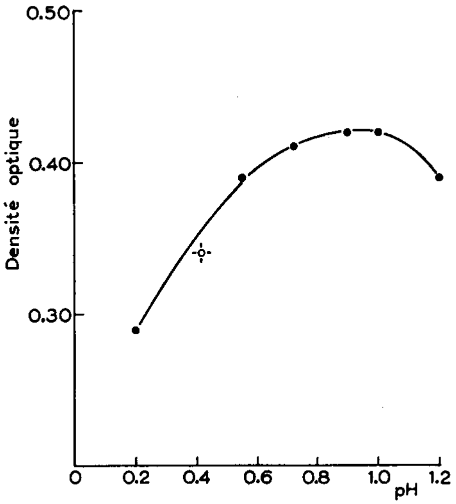

Fig. 2. Influence du pH sur l'extraction.

Influence et choix de la concentration du colorant

La concentration du colorant utilisée pour l'extraction influe doublement sur le résultat final. En effet le rendement de l'extraction dépend directement de cette concentration et nous avons montré qu'elle doit être suffisamment élevée pour que la quantité extraite soit négligeable devant la quantité totale. Mais ce qui précède montre d'autre part que la concentration du cation coloré HB^+ dans la phase aqueuse de lavage à l'équilibre dépend principalement du déplacement de l'équilibre II dans

TABLEAU I

Concentration du colorant au moment de l'extraction	*Densité optique de l'essai à blanc après lavage par HCl 0.65N*	*Densité optique de la phase organique après lavage par HCl 0.65N pour 6 μg d'étain*	*Différence*
$7.5 \cdot 10^{-4}$	0.19	0.95	0.76
$1.5 \cdot 10^{-3}$	0.32	1.17	0.85
$3 \cdot 10^{-3}$	0.51	1.46	0.95

le sens 2. Elle est donc fonction de la concentration initiale du chlorhydrate dans la phase organique et dépend finalement de la concentration du colorant au moment de l'extraction. Les résultats rassemblés dans le tableau ci-dessous montrent l'influence de cette concentration sur la valeur de l'essai à blanc et sur la sensibilité du dosage.

Nous avons adopté arbitrairement la concentration $1.5 \cdot 10^{-3}$ de manière à obtenir un essai à blanc de densité optique peu élevée (0.32).

Influence du pH

Les réactions III et IV montrent que la stabilité du complexe $SnCl_4^{-2}$ est fonction de la concentration des chlorures et du pH. Nous avons montré dans le mémoire précédent que la concentration du cation coloré HB^+ dépend également du pH. Pour étudier l'influence de ce facteur, il est donc nécessaire de maintenir constante la concentration des chlorures, en mélangeant par exemple des solutions de chlorure de potassium et d'acide chlorhydrique. En utilisant une concentration élevée de chlorure ($1M$) dans le but de stabiliser le complexe, l'expérience montre que le rendement de l'extraction passe par un maximum entre pH = 0.9 et pH = 1. La courbe obtenue est représentée sur la Fig. 2. La densité optique portée en ordonnées correspond à 3 μg d'étain extrait par 5 ml de solvant. On remarque que cette courbe est presque identique à celle qui figure dans le mémoire précédent, ce qui parait logique puisque les deux colorants utilisés sont très voisins. Mais, en présence d'une concentration moléculaire de chlorure, la densité optique de l'essai à blanc est trop élevée (0.70 à

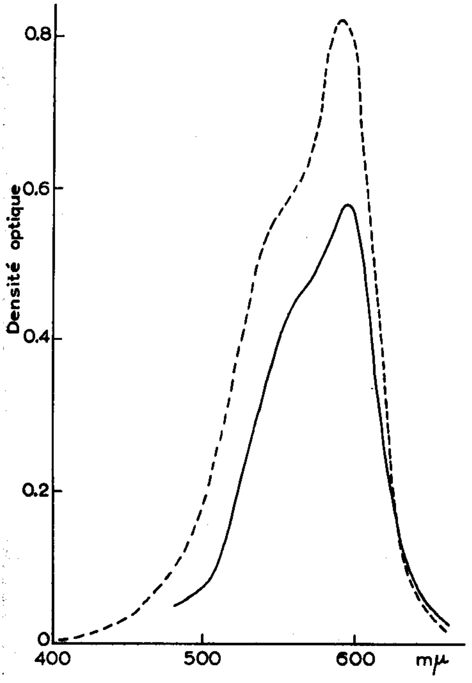

Fig. 3. Spectres d'absorption: . . . . : de la molécule de „Violet Cristallisé" en solution aqueuse (4 mg/l); ——: du complexe dans la 4-heptanone.

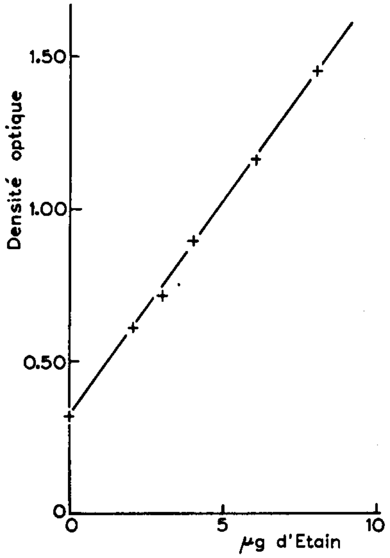

Fig. 4. Courbe d'étalonnage: pour le dosage de l'étain.

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pH = 0.9) pour que ces conditions soient utilisées pratiquement. Nous avons donc recherché la sensibilité optimum en fonction de la concentration de l'acide chlorhydrique seul. Le meilleur résultat est obtenu pour un titre égal à 0.3*N*, soit pour pH = 0.65 environ. La sensibilité obtenue dans ces conditions est voisine de celle des essais précédents effectués à pH = 0.9 en présence d'une concentration moléculaire des chlorures, mais la densité optique de l'essai à blanc est plus faible : 0.30 environ.

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Maroc". Les courbes de la Fig. 3 représentent les spectres d'absorption de la molécule de colorant en milieu aqueux et de la combinaison extraite par la butyrone. On voit que ces spectres sont très voisins et que le maximum d'absorption de la combinaison est situé à 595.0 mμ.

La loi de Beer est suivie, à ±2% près, même pour des valeurs de la densité optique de l'ordre de 1.50, comme le montre la courbe de la Fig. 4 obtenue avec une cuve d'une épaisseur de 1 cm. Ces résultats permettent de calculer un coefficient d'extinction moléculaire apparent: il est de 85.000 à 20°.

MODE OPÉRATOIRE

Pour 5 ml d'une solution d'étain dans l'acide chlorhydrique normal: dans une ampoule à décanter de 125 ml, non graissée, verser dans l'ordre: 5 ml de la solution à doser, 5 ml de soude 0.5*N*, 5 ml de solvant, 5 gouttes de la solution de cupferron (0.25 ml environ), 3 ml de la solution de colorant; homogéniser puis ajouter 2 ml de la solution diluée de chlorure titaneux. Agiter énergiquement durant 5 min. exactement, puis laisser décanter. Dès que les deux phases sont séparées, éliminer la couche aqueuse inférieure. Verser ensuite dans l'ampoule 10 ml de la solution de lavage (acide chlorhydrique 0.65*N*), puis agiter durant 1 min. Aussitôt après décantation, effectuer la colorimétrie de la phase organique à 595.0 mμ.

Essai à blanc

Opérer de la même manière en remplaçant la solution à doser par 5 ml d'acide chlorhydrique normal.

Courbe d'étalonnage

Remplacer dans le mode opératoire la solution à doser par 5 ml d'une solution chlorhydrique normal renfermant une quantité connue d'étain.

Précautions

(a) le colorant étant lentement détruit en milieu acide à la lumière, la durée d'un dosage doit-être de l'ordre de 15 min.

(b) Un faible abaissement de la température de la phase organique après extraction et lavage (de l'ordre du 1/2 degré) provoque un trouble dû vraisemblablement à la formation de fines gouttelettes d'eau. Ce phénomène que nous avons observé avec d'autres solvants est réversible; un léger réchauffement suffit pour obtenir une solution limpide.

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Influence de quelques ions

La présence des anions SO_4^{-2} et NO_3^- ne pertube pas le dosage; la sensibilité de la méthode ne varie pas; seule la densité optique de l'essai à blanc est modifiée. Par exemple pour une concentration des anions SO_4^{-2} ou NO_3^- égale à $5 \cdot 10^{-2}$, la densité optique de l'essai à blanc devient voisine de 0.50.

Certains cations qui présentent des complexes chlorhydriques comme: Sb(III), Tl(III), Bi(III), Cu(II) gênent car ils sont extractibles; d'autres comme Ge(IV), As(III), Pb(II), Co(II), Zn(II), Cr(III), ne modifient pas les résultats même si leur concentration est égale à 10^{-3}.

REMARQUES

(1) La butyrone peut-être remplacée par l'hexone, mais le rendement de l'extraction diminue: le coefficient d'extinction moléculaire apparent devient voisin de 30.000 à 20°.

(2) Le complexe oxalique de Sn(IV) associé au bleu de méthylène est extractible par le mélange acétophénone – 1,2-dichloréthane, mais une quantité importante d'oxalate de bleu de méthylène est extraite simultanément. Il est ensuite difficile de l'éliminer par lavage sans détruire la plus grande partie de la combinaison stannique.

RÉSUMÉ

Le complexe stannochlorhydrique $SnCl_4^{-2}$, associé au cation du violet cristallisé, est extractible vers pH = 1 par la 4-heptanone ou butyrone. L'extraction simultanée d'une petite quantité de chlorhydrate du colorant entraine un ,,lavage'' de la phase organique par une solution d'acide chlorhydrique. Cette opération diminue la sensibilité, mais le coefficient d'extinction moléculaire apparent est encore très grand puisqu'il est voisin de 85.000.

SUMMARY

An extraction method is described for the determination of traces of tin in which crystal violet is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren-Mengen von Zinn mit Hilfe von Kristallviolett nach dem Extraktionsverfahren.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION A L'AIDE DE COLORANTS BASIQUES

C. DOSAGE DE TRACES DE PHOSPHATE PAR LA SAFRANINE

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BUT ET PRINCIPE

Pour certaines recherches dans le domaine des semi-conducteurs, la sensibilité des méthodes classiques de dosage de traces de phosphate est insuffisante (complexe phospho-vanado molybdique, réduction du complexe phosphomolybdique). Nous avons pensé que l'utilisation d'un colorant basique permettrait d'améliorer la sensibilité, et d'atteindre celle des méthodes radiochimiques lorsqu'elles sont appliquées au cas défavorable du silicium, en présentant l'avantage d'une plus grand rapidité d'exécution.

Les anions phosphates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Les phosphomolybdates et les phosphotungstates donnent avec des colorants basiques des groupes des azines, des thiazines et du triphénylméthane, des combinaisons peu solubles dans l'eau et dans les liquides organiques les plus courants. Cependant certains colorants comme le rouge neutre et la safranine associés à ces anions donnent à un pH convenable une combinaison extractible par quelques cétones aromatiques en particulier par l'acétophénone. Ce liquide possède une viscosité assez élevée et une densité voisine de celle de l'eau qui rend difficile la séparation des phases. On peut modifier ces propriétés par addition d'un solvant chloré peu volatil comme l'*o*-dichlorobenzène sans modifier profondément les phénomènes de solvatation.

Le molybdate ajouté en excès pour former l'anion phosphomolybdique précipite presque totalement le colorant. Mais l'expérience montre que le précipité très peu soluble dans la phase organique, se rassemble lors de l'extraction à l'interface et ne gêne pas dans certaines conditions la reproductibilité des résultats. Toutefois la loi de Beer n'est pas suivie; il est donc nécessaire d'établir une courbe d'étalonnage.

ÉTUDE DES DIFFÉRENTS FACTEURS DU DOSAGE

Réactifs utilisés

Acide sulfurique pour toxicologie. Solvant. C'est un mélange renfermant trois volumes d'acétophénone pour un volume d'*o*-dichlorobenzène. Ces deux liquides sont préalablement rectifiés sous vide dans un appareil en verrerie rodée, non graissée.

Solution de molybdate. Solution aqueuse $10^{-3}M$ de molybdate d'ammonium R.P. [$(NH_4)_6 Mo_7O_{24}$, 4 H_2O], soit 1.25 g/l.

Solution de safranine. Solution aqueuse à 2 g/l du produit R.A.L. pour microbiologie. La solution agitée pendant 30 min est ensuite filtrée sur un creuset de verre fritté No. 2.

Solution étalon de phosphate. On prépare une solution-mère renfermant 300 μg de phosphore par ml, à l'aide de phosphate disodique R.P. (Na_2HPO_4, 12 H_2O), soit 3.47 g/l. Par dilution avec de l'eau distillée, on obtient une solution étalon renfermant 0.6 μg de phosphore par ml.

Influence du pH

Plusieurs facteurs dépendent du pH:

- la solubilité du précipité de molybdate de safranine,
- l'existence du cation coloré HB^+. Nous avons montré dans les mémoires précédents qu'il n'existe qu'en milieu acide.
- la stabilité du complexe phosphomolybdique.

La variation du pH est obtenue par addition d'acide sulfurique; les autres facteurs sont maintenus constants: phosphate ajouté (2 ml de la solution étalon, soit 1.2 μg de phosphore), volume de la solution de molybdate (4 ml) et de la solution de safranine (1 ml), volume total de la phase aqueuse (20 ml) et de la phase organique (10 ml), température (20°), temps d'agitation (5 min).

Les résultats sont représentés par la courbe de la Fig. 1; la densité optique portée en ordonnées représente la différence entre la densité optique de l'essai renfermant 1.2 μg de phosphore ajouté et celle de „l'essai à blanc" effectué dans les mêmes conditions (les 2 ml de la solution étalon sont remplacés par de l'eau distillée). La cuve a 1 cm d'épaisseur, on voit que le maximum de sensibilité est atteint dans un domaine de pH restreint, entre pH = 1.4 et pH = 1.6.

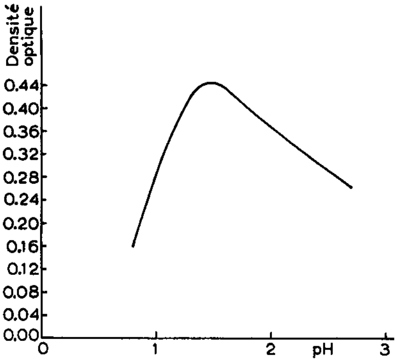

Fig. 1. Influence du pH sur l'extraction du phosphomolybdate de safranine (1,2 μg de phosphore).

Spectrophotométrie

L'appareil utilisé est le spectrophotomètre Jobin et Yvon, type „Algérie".

L'essai à blanc présente une densité optique assez élevée, de l'ordre de 1,5 unités; cette coloration provient des traces de phosphate que renferment les réactifs et d'une légère solubilité du précipité de molybdate de safranine. Cette valeur est trop grande pour permettre une spectrophotométrie directe, mais suffisamment faible pour qu'une spectrophotométrie différentielle soit possible. L'essai à blanc est donc utilisé pour le réglage du zéro de l'appareil de mesures (densité optique = 0; transmission = 100).

L'expérience montre d'autre part que les résultats ne sont reproductibles (à 0.02 unité de densité optique près) que si l'on abandonne le précipité de molybdate de safranine pendant au moins 10 min avant l'extraction.

Le spectre d'absorption du phosphomolybdate de safranine dans le solvant et celui de la molécule du colorant dans l'eau sont représentés sur la Fig. 2. La densité optique de la phase organique est mesurée au maximum d'absorption, soit pour $\lambda = 532.5$ mμ.

La loi de Beer n'est pas suivie : la courbe d'étalonnage de la Fig. 3 montre que la sensibilité augmente avec la quantité de phosphate extrait.

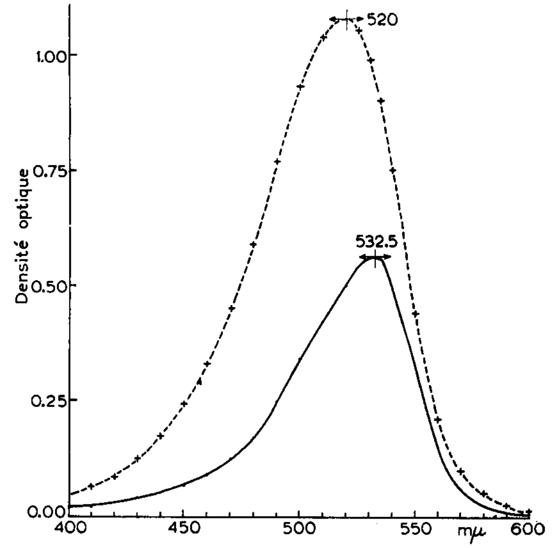

Fig. 2. Spectres d'absorption: .... de la safranine dans l'eau; —— du phosphomolybdate de safranine dans le solvant.

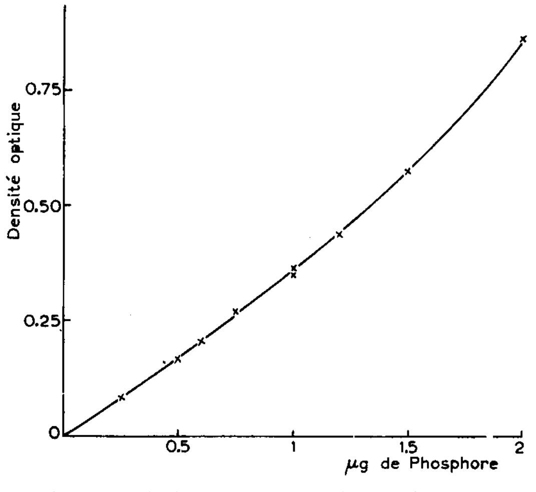

Fig. 3. Courbe d'étalonnage pour le dosage du phosphore.

La réaction d'extraction est pratiquement quantitative comme le prouve l'expérience suivante : on compare la densité optique d'un essai renfermant 1.2 µg de phosphore à celle de l'essai à blanc. D'après la courbe d'étalonnage de la Fig. 3, la différence est voisine de 0.44. Les deux phases aqueuses renfermant le précipité sont recueillies et une seconde extraction est effectuée dans les mêmes conditions. Les deux phases organiques obtenues présentent alors la même densité optique, qui en valeur absolue est inférieure d'environ 40% à celle de l'essai à blanc initial. Ceci prouve d'une part qu'une seule opération suffit pour que la réaction d'extraction soit quantitative d'autre part que la coloration obtenue après la seconde opération provient d'une légère solubilité du précipité de molybdate de safranine.

Bien que la loi de Beer ne soit pas suivie, on peut calculer un coefficient d'extinction moléculaire moyen pour une quantité donnée de phosphore extrait. D'après la courbe d'étalonnage, on obtient par exemple 116.000 entre 0 et 1 µg et 155.000 entre 1 et 2 µg. Il est d'ailleurs possible d'utiliser cette dernière sensibilité; il suffit, d'ajouter 1 µg de phosphore à l'essai à blanc et à la solution à doser. La Fig. 4 présente une courbe d'étalonnage obtenue dans ces conditions: on voit que la courbe devient pratiquement rectiligne lorsque la quantité de phosphore extrait augmente; le coefficient d'extinction moléculaire correspondant à cette partie de la courbe est voisin de 190.000.

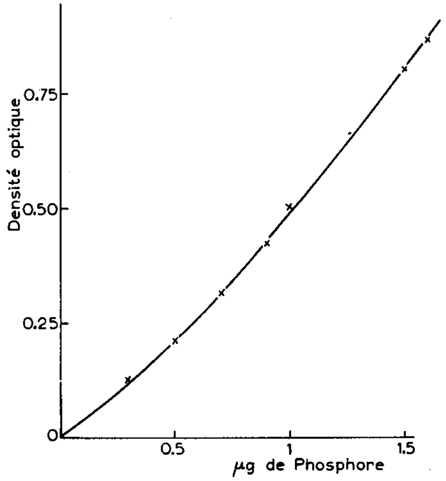

Fig. 4. Courbe d'étalonnage après addition de 1 µg de phosphore.

Concentration du molybdate et du colorant

Les volumes des solutions de molybdate et de safranine sont choisis de manière qu'il reste dans la phase aqueuse après la formation du précipité un large excès de molybdate pour la formation du complexe phosphomolybdique.

Au pH optimum (1.5), le précipité n'est que légèrement soluble, la concentration du cation coloré est donc très faible. Malgré ces conditions apparemment défavorables, l'expérience montre que l'extraction est quantitative.

Influence de quelques ions

Le dosage peut-être effectué en présence de chlorures. Par contre les anions minéraux suivants sont extraits: arséniate, arsénite, vanadate, perchlorate, nitrate ainsi que certains anions organiques: thiocyanate, trichloracétate.

En milieu chlorhydrique, les cations donnant des complexes du type ACl_4^- gênent car ils sont extraits: Au(III), Bi(III), Tl(III), Sb(III).

MODE OPÉRATOIRE

Nous avons adopté le mode opératoire suivant:

Placer dans une ampoule à décantation de 125 ml non graissée 5 ml de la solution neutre de phosphate à doser, 10 ml d'acide sulfurique *N*/10, 4 ml de la solution de molybdate, 1 ml de la solution de safranine. Homogénéiser, abandonner durant 10 min. Ajouter ensuite 10 ml de solvant; agiter énergiquement durant 5 min. Après décantation (15 min. environ), recueillir la majeure partie de la phase organique et la centrifuger. Effectuer immédiatement la spectrocolorimétrie différentielle à 532.5 mμ en cuve de 1 cm, en règlant le zéro de l'appareil de mesures à l'aide d'un essai à blanc effectué *parallèlement* dans des conditions identiques en remplaçant la solution de phosphate à doser par 5 ml d'eau distillée.

La courbe d'étalonnage est obtenue en remplaçant la solution à doser par une solution renfermant une quantité connue de phosphore.

Précautions

(a) L'expérience montre que la densité optique de la phase organique diminue lentement avec le temps (environ 2/100 d'unité de densité optique par heure). Il est donc recommandé d'une part, d'effectuer en parallèle le dosage et l'essai à blanc et d'autre part, d'effectuer la mesure des densités optiques immédiatement après la centrifugation.

(b) Comme nous l'avons déjà indiqué dans le mémoire précédent, un léger abaissement de la température provoque l'apparition d'un trouble dans la phase organique, dû à la formation de fines gouttelettes d'eau. Un léger réchauffement rend à la solution sa limpidité.

RÉSUMÉ

Les anions phosphates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Par contre, les phosphomolybdates associés à certains colorants sont extractibles par des cétones aromatiques. Avec la safranine l'extraction par l'acétophénone est quantitative à pH = 1.5. Il est nécessaire d'établir une courbe d'étalonnage, la loi de Beer n'étant pas suivie. La sensibilité est très grande; une partie de la courbe d'étalonnage présente un coefficient d'extinction moléculaire moyen voisin de 190.000.

SUMMARY

An extraction method is described for the determination of traces of phosphate in the form of phosphomolybdate, in which safranine is used as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode beschrieben zur Bestimmung von Spuren-Mengen von Phosphat in Form von Phosphormolybdat mit Hilfe von Safranin nach dem Extraktionsverfahren.

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DOSAGES EN ANALYSE MINÉRALE PAR EXTRACTION À L'AIDE DE CATIONS COLORÉS

III. DOSAGES PAR EXTRACTION À L'AIDE DE COLORANTS BASIQUES

D. DOSAGE DE TRACES DE SULFATE PAR LE BLEU DE MÉTHYLÈNE

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PRINCIPE

Nous avons essayé d'appliquer au dosage de traces de sulfate la méthode développée dans les mémoires précédents : associer à l'anion à doser le cation d'un colorant basique pour former une combinaison extractible par un solvant convenablement choisi. De nombreux colorants des groupes des azines, thiazines, triphénylméthane ont été essayés sans succès. La propriété que présente l'ion sulfate de donner des composés peu solubles dans l'eau avec certaines diamines ou polyamines primaires de masse moléculaire élevée, comme la benzidine et ses dérivés, se retrouve avec les colorants basiques : la thionine ou violet de Lauth, le brun Bismarck par exemple précipitent quantitativement avec les ions sulfates, mais nous n'avons pas trouvé le solvant approprié.

Nous avons alors pensé qu'il était possible de développer une méthode générale permettant de substituer aux anions à doser non extractibles comme les ions sulfates, des anions facilement extractibles en utilisant une résine anionique. Nous avons choisi l'ion thiocyanate qui présente moins d'affinité pour les résines que l'ion sulfate, et qui associé aux cations de nombreux colorants basiques donne des combinaisons facilement extractibles. Par exemple, avec le bleu de méthylène la combinaison est soluble dans le dichloro-1,2-éthane.

La réaction utilisée s'écrit:

$$\underset{\text{résine}}{2\,\text{CNS}^-} + \underset{\text{solution}}{\text{SO}_4^{-2}} \rightleftharpoons \underset{\text{résine}}{\text{SO}_4^{-2}} + \underset{\text{solution}}{2\,\text{CNS}^-}$$

DOSAGE DES IONS THIOCYANATES PAR LE BLEU DE MÉTHYLÈNE

L'anion CNS^- associé au bleu de méthylène est extractible quantitativement en milieu acide (vers $\text{pH} = 1$) par le dichloro-1,2-éthane. Nous avons adopté le mode opératoire suivant:

Réactifs utilisés

Ils sont préparés avec de l'eau bidistillée dans un appareil en quartz.

Acide sulfurique 2N/10.

Solution de colorant. Solution aqueuse à 3 g/l du produit R.A.L. médicinal; la solution agitée pendant 30 min est ensuite filtrée sur creuset de verre fritté No. 2.

Dichloro-1,2-éthane. Le produit commercial pur est lavé deux fois dans une ampoule à décanter pendant quelques minutes par son demi-volume de soude normale, puis par son volume d'eau distillée. Il est ensuite distillé dans un appareil en verrerie rodée non graissée; on recueille la fraction distillant à 83° ± 1°.

Mode opératoire

Dans une ampoule à décanter de 125 ml non graissée, placer 10 ml de solvant, 5 m d'acide sulfurique $2N/10$, 1 ml de solution du colorant et 5 ml de la solution à doser. Agiter énergiquement pendant 3 min. Laisser décanter, puis séparer la couche organique et la centrifuger. Mesurer la densité optique pour $\lambda = 660.0$ mμ.

„L'essai à blanc" est effectué dans les mêmes conditions en remplaçant la solution à doser par de l'eau bidistillée. Il présente une densité optique voisine de 0.50 qui est due à une légère solubilité du sulfate de bleu de méthylène.

La Fig. 1 représente la droite d'étalonnage obtenue en remplaçant dans le mode opératoire la solution à doser par une solution de thiocyanate de potassium (R. P Prolabo) de titre connu. Les densités optiques (cuve de 1 cm) figurent en ordonnées et les concentrations des solutions de thiocyanate de potassium utilisées en abscisses. L'appareil utilisé est le spectrophotomètre Jobin et Yvon type „Algérie". Le coefficient d'extinction moléculaire est voisin de 74.000.

Préparation de la résine. Essai à blanc

Nous avons utilisé la résine Dowex-1 X 4, 200 – 400 mesh commercialement sous forme de chlorure. Elle est traitée de la façon suivante : 30 g de résine humide sont agités dans un flacon pendant 20 min. avec deux fois 50 ml de solution $N/10$ de thiocyanate de potassium R. P., puis trois fois avec 50 ml de solution $2N$. La résine est filtrée et lavée à l'eau distillée entre chaque agitation. Elle est ensuite agitée de la même façon quatre fois avec 100 ml d'eau distillée, filtrée et abandonnée durant 48 heures dans l'eau distillée.

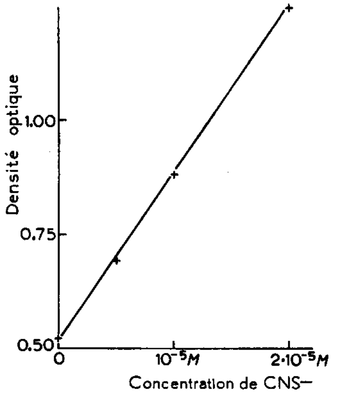

Fig. 1. Courbe d'étalonnage pour le dosage du thiocyanate.

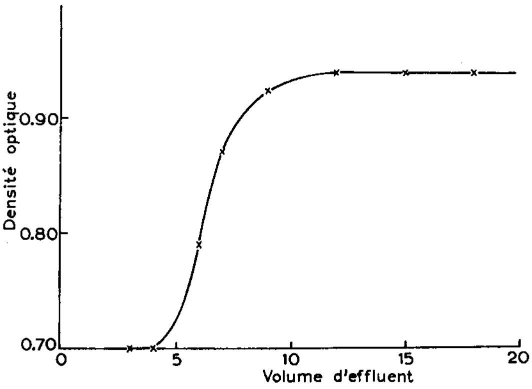

Fig. 2. Variation de la concentration du thiocyanate dans l'effluent en fonction du volume écoulé.

La résine est ensuite placée dans une colonne d'un diamètre de 1 cm, sur une hauteur de 15 cm. On fait ensuite passer sur la colonne de l'eau bidistillée (dans un appareil en quartz) par portion de 25 ml. La compacité du remplissage de la colonne est telle que le robinet étant ouvert au maximum, le débit est suffisamment lent : 25 ml en 15 min. On recueille les 5 derniers ml de chaque portion et l'on dose les ions thiocyanates par la méthode indiquée ci-dessus. Le lavage est poursuivi tant que la densité optique de ce dosage décroit. Elle doit ensuite rester constante à 0.01 unité près, si l'on observe les précautions relatives aux variations de température indiquées ci-dessous.

Nous avons trouvé la densité optique de l'essai à blanc à 21° égale à 0.81 ± 0.01.

Étalonnage. Dosage des traces de sulfate

Une solution de sulfate de potassium exactement $10^{-2}M$ est préparée par pesée du sel Prolabo R. P. Par dilution on obtient une gamme de solutions dont les titres s'échelonnent entre 10^{-6} et $2 \cdot 10^{-5}$ M.

On trace ensuite la courbe représentant les variations de la concentration des ions thiocyanates dans l'effluent en fonction du volume, lorsqu'une solution de sulfate traverse la colonne. La courbe de la Fig. 2 a été obtenue de la manière suivante: on fait affleurer le niveau de l'eau distillée restant dans la colonne juste à la partie supérieure de la résine; on introduit ensuite dans la colonne avec précautions 25 ml d'une solution $10^{-5}M$ de sulfate. On recueille l'effluent par portions de 3 ml, et l'on effectue le dosage des ions thiocyanates. Afin de ne pas modifier le mode opératoire décrit ci-dessus on ajoute 2 ml d'eau bidistillée aux 3 ml d'effluent. Les densités optiques sont portées en ordonnées, le volume d'effluent en abscisses. Les premières portions recueillies présentent une densité optique de 0.70, valeur de l'essai à blanc pour 3 ml de solution. Le volume d'effluent correspondant à cette valeur (4 ml environ) représente la somme du volume interstitiel et du volume mort à la partie inférieure de la colonne. Cette courbe permet de déterminer à partir de quel volume la concentration des ions thiocyanates est constante. On peut donc éliminer la première partie de l'effluent, et ne conserver pour le dosage que le volume correspondant à la concentration maximum.

Nous avons finalement adopté le mode opératoire suivant valable pour l'étalonnage et le dosage d'une solution inconnue:

Faire affleurer le niveau de la solution restant dans la colonne juste à la partie supérieure de la résine. Introduire avec précautions 25 ml de la solution à doser (ou de la solution de titre connu). Recueillir les quinze premiers ml, les rejeter,

TABLEAU I

Concentration des solutions de sulfate	*Temp. = 21°*	*Densité optique colorimétrie différentielle cuve de 1 cm*
0		0
$10^{-6}M$		0.045 0.052
$2 \cdot 10^{-6}M$		0.105 0.117
$5 \cdot 10^{-6}M$		0.250 0.255
$10^{-5}M$		0.495 0.510
$2 \cdot 10^{-5}M$		0.97 0.98

recueillir ensuite les dix derniers ml dans un récipient propre et sec. Prélever 5 ml et doser les ions thiocyanates comme il est indiqué ci-dessus.

La densité optique de l'essai à blanc étant élevée (0.80 environ) il est préférable d'effectuer une colorimétrie différentielle pour $\lambda = 660.0$ mμ en règlant le zéro de l'appareil à l'aide de cet essai (transmission = 100, densité optique = 0).

Les résultats sont rassemblés dans le Tableau I.

Influence de la température.

La reproductibilité des résultats dépend essentiellement de la température. Il est indispensable que les solutions utilisées soient amenées à la température du laboratoire. Celle-ci doit-être constante à 0.5° près. Il faut soustraire la colonne à tout rayonnement thermique: rayons solaires étuve, ampoule électrique, etc. On peut l'isoler à l'aide d'un enroulement de toile d'amiante par exemple.

RÉSUMÉ

Les ions sulfates ne semblent pas donner avec les colorants basiques des combinaisons extractibles. Une méthode générale, utilisant une résine anionique permet de substituer aux anions à doser non extractibles comme les sulfates, des ions facilement extractibles comme les thiocyanates: la solution diluée de sulfate passe sur une colonne de résine Dowex-1 X 4 préalablement mise sous forme thiocyanate. Les ions thiocyanates libérés, associés aux cations du bleu de méthylène sont extractibles quantitativement à pH = 1 par le dichloro-1,2-éthane. La méthode permet de doser des concentrations très faibles de sulfate ($10^{-6}M$).

SUMMARY

A method is described for the determination of traces of sulphate. By means of an exchange resin the sulphate ions are exchanged with an equivalent amount of thiocyanate ions and these are determined by the extraction method using methylene blue as complexing agent.

ZUSAMMENFASSUNG

Es wird eine Methode zur Bestimmung von Spuren-Mengen Sulfat beschrieben. Das Sulfat-Ion wird mit Hilfe eines Austauscher-Harzes gegen eine äquivalente Menge Thiocyanat-Ion ausgetauscht und dieses mit Methylenblau nach dem Extraktionsverfahren bestimmt.

Reçu le 15 octobre 1958

Short Communications

Detection of the heavier rare-earth metal ions with several organic reagents

In previous studies, the detection of the lighter trivalent rare-earth ions with oxalic acid, cupferron, 8-quinolinol, and 2-methyl-8-quinolinol was reported[1,2]. Since only the rare-earth ions from lanthanum to gadolinium were studied, this investigation reports the detection of the heavier rare-earth ions with the same reagents.

The procedure for the sensitivity tests was essentially a modification of the method of IRVING, BUTLER, AND RING.[3] Tests were conducted in 15 by 145 mm test tubes containing a known amount of 0.01 M or 0.001 M rare-earth metal chloride solution. For the oxalic acid and cupferron tests, 0.2 ml of 0.1 M reagent was added to the rare-earth solutions, diluted with water to 7.0 ml, and then heated for 10 min at 70°. The solutions were allowed to cool to room temperature and observed visually for the presence of a precipitate. A similar procedure was followed for the 8-quinolinol and 2-methyl-8-quinolinol tests except that 0.2 ml of the 0.1 M reagent in 95% ethanol was added to the rare-earth solutions containing 2.0 ml of an NH_4Cl–NH_4OH buffer, and then diluted with water to a total volume of 7.0 ml. The pH of the resulting solution was 9.5.

TABLE I

RESULTS OF SENSITIVITY TESTS

Metal ion	*µg M^{+3} per ml*			
	Oxalic acid	*Cupferron*	*8-Quinolinol*	*2-Methyl 8-quinolinol*
Europium	35	5.2	1.7	17
Terbium	36	7.1	1.4	7.1
Dysprosium	19	7.4	1.1	7.4
Holmium	38	13	3.8	13
Erbium	57	17	3.8	9.5
Ytterbium	40	30	4.0	20

The results of the sensitivity tests are given on Table I. By far the best reagent for the detection of the rare-earth ions was 8-quinolinol. The decrease in sensitivity on introduction of a 2-methyl-group on the 8-quinolinol nucleus may be attributed to either a steric hindrance[3] or a solubility effect.

The detection of the rare-earth ions with cupferron compares favorably with 2-methyl-8-quinolinol. However, the tests with cupferron were conducted in neutral solutions. The sensitivity of cupferron to detect the rare-earth ions was much greater than that found for oxalic acid. In fact, of all the reagents studied, oxalic acid was the least sensitive. It is to be expected that the sensitivity of oxalic acid would decrease with increasing hydrogen ion concentration while the sensitivity of the cupferron test would remain about the same.

As a general observation, the sensitivity of the tests decreased with increase in atomic number of the rare-earth metal ion. This decrease in sensitivity is quite prominently shown in going from the lighter[1,2] to the heavier rare-earths.

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Lubbock, Texas (U.S.A.)

WESLEY W. WENDLANDT
ROGER G. SEWELL

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[1] W. W. WENDLANDT, *Science*, 125 (1957) 1042.
[2] W. W. WENDLANDT AND D. W. HAYES, *Science*, 126 (1957) 451.
[3] H. IRVING, E. J. BUTLER AND M. F. RING, *J. Chem. Soc.*, (1949) 1489.

Received April 9th, 1959

A convenient boiling tube for the safe and steady boiling of solutions

The prolonged boiling of many solutions is often a risky or, at best, a troublesome procedure. Boiling stones, glass beads, marble chips, granules, pebbles, etc., are frequently used in an effort to obtain a more even boiling action and thereby prevent the loss of sample by bumping. However, such devices do not always produce the desired result.

A simple but more effective device for the quiet and safe boiling of solutions, with a minimum amount of manipulation, is a specially-designed boiling tube which may be prepared in any laboratory. Analysts, to whom this accessory has been demonstrated, consider it preeminent as a boiling aid.

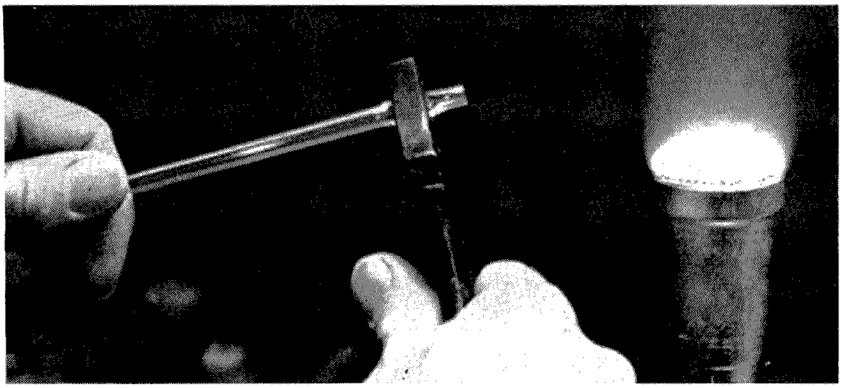

Fig. 1.

Procedure

Obtain a glass tube, preferably one of soft glass, 6 mm in outside diameter and about 8 in. long. After fire-polishing the ends, heat one end until about 1" of it is soft. Immediately thereafter, with the aid of pliers, form a seal by pinching the tube completely closed at one spot about 1/4 in. to 1/2 in. from the heated end (see photograph). Allow the tube to cool.

To use, place the constricted portion of the tube in the solution, touching the edge of the boiling-vessel bottom. A bubble of air should be trapped in the small open section of the tube below the seal. Now heat the solution. When the boiling point is reached, the lower open end of the tube will act as a source from which gases, produced by the boiling, may escape. A very satisfactory boiling action ensues. When the boiling operation is complete, the tube can be easily removed and then rinsed in a matter of seconds.

Chemical-Pigments-Metals Division,
The Glidden Company,
Baltimore, Md. (U.S.A.)

HARRY M. PUTSCHÉ

Received March 13th, 1959

REVUE DE LIVRE

Traité de micro-analyse minérale par **CLÉMENT DUVAL**, tome III, 1956, 548 pp., Prix 3,600 Fr., tome IV, 1957, 892 pp., Prix 3,600 Fr., Presses scientifiques internationales, Paris, 1956 et 1957.

Les 4 volumes de ce bel ouvrage sont maintenant sortis de presse. Nous avons déjà présenté le tome I et le tome II. Les tomes III et IV comprennent comme les précédents un élément par chapitre. L'exposé est clair, dans un ordre parfaitement logique, ce qui rend la consultation de ce traité particulièrement agréable et aisée.

Le tome III renferme les éléments des colonnes VIIIa, Ib et IIb du système périodique, soit les éléments de numéro atomique 26 à 30, 44 à 48 et 76 à 80. Au total 15 éléments. Le tome IV traite des éléments des colonnes IIIb, IVb, Vb, VIb, VIIb et 0, soit en tout 31 éléments.

L'auteur est bien modeste lorsqu'il intitule son ouvrage: „*Traité de micro-analyse minérale*", car, en fait, il a largement dépassé ce cadre et on trouve dans son livre une foule de documents sur tout le domaine de l'analyse minérale. En particulier, il donne de nombreux renseignements sur l'analyse de traces et sur l'ultramicroanalyse.

On ne saurait trop féliciter **CLÉMENT DUVAL** pour le choix des méthodes qu'il nous propose et spécialement de l'énorme travail de bibliographie que lui et ses collaborateurs se sont imposés et grâce auquel cet ouvrage est l'un des plus documentés et des plus complets dans ce domaine de l'analyse. Pour le cobalt, par exemple, on trouve 389 références, 311 pour le nickel, 745 pour le cuivre et ainsi de suite. On comprend dès lors le succès qu'il a rencontré; il rend et rendra à tous ceux qui de près ou de loin s'intéressent à la chimie analytique minérale, les plus grands services)

D. MONNIER (Genève.

BOOK REVIEW

Precipitation from Homogeneous Solution, by **L. GORDON, M. L. SALUTSKY AND H. H. WILLARD.** John Wiley & Sons Inc. New York 1959, 187 pages. $ 7.50.

It is refreshing to read a current publication dealing with an important aspect of 'classical' methods of analysis, which tends to confirm that the craftmanship associated with this branch of chemistry has still an important part to play, despite all the recent advances in instrumental method of analysis.

The publication can be divided into two sections, dealing first with practical applications of homogeneous precipitation, then, commencing with Chapter 8, a theoretical approach to the subject is made; the reason for this reversal of customary practice is not obvious.

As a source of reliable information on the subject of homogeneous precipitation, the book can be recommended, but the analyst is invariably left to speculate as to the real purpose for which the recommended procedures are intended. Many of the procedures are inordinately time consuming, e.g. on page 47 the statement is made that 'quantitative precipitation of zirconium requires 18 to 24 hours at the boiling point'; in other instances, procedures can only be applied in the absence of a large range of elements, an ideal state of affairs rarely, if ever, the lot of the analyst. It is difficult to appreciate the value of the recommended method for determining gallium, based on precipitation of what is, presumably, basic gallium sulphate, brought about by the slow hydrolysis of urea, when it is known that many metals are also precipitated under similar conditions. The authors do, however, recommend that the determination of gallium should be completed colorimetrically, but in this, as in other methods, there is no obvious reason why determination of the metal in question should not be made direct in the first instance.

The book is written in a very clear style.

The underlying principle of homogeneous precipitation is governed by the factors embodied in the **VON WEIRMANN** equation and it is disappointing to find that this relatively simple equation does not appear anywhere in the book.

This critical survey should not detract from the value of the adequate coverage the authors have given to the subject of homogeneous precipitation, particularly for the analyst who has a use for this fascinating technique.

W. J. ELWELL (Birmingham)

BUCHBESPRECHUNG

Qualitative Analyse, von N. I. BLOK, VEB, Deutscher Verlag der Wissenschaften, Berlin, 1958, (das Buch ist eine Übersetzung und deutsche Bearbeitung des 1952 in russischer Sprache in Moskau und Leningrad herausgekommenen Buches) 574 S., 59 Abb., 60 Tabellen, DM 36.—.

Bei diesem als Lehrbuch für Studenten gedachten Werk handelt es sich nicht um ein Lehrbuch der praktischen Analyse, wie der Titel vielleicht vermuten läßt. Der ganzen Anlage nach würde ein Titel wie *Einführung in die anorganische und allgemeine Chemie an Hand der chemischen Analyse* dem Inhalt besser gerecht werden. Das Hauptanliegen des Buches ist es, die Grundlagen für einen Unterricht zu geben, bei dem der Student in erster Linie mit den chemischen Eigenschaften der Stoffe in wäßrigen Lösungen bekannt gemacht werden soll. Hierzu wird, wie das seit langem üblich und verbreitet ist, in erster Linie von solchen Reaktionen ausgegangen, die analytisch angewendet werden.

Dasjenige, was das hier vorliegende Buch von vielen Büchern ähnlicher Zielsetzung unterscheidet, ist, daß mit großer Konsequenz versucht worden ist, den Benutzer dadurch zu einem tieferen Verständnis und auch zu einer besseren und leichteren Übersicht zu führen, daß das analytisch Interessierende und das allgemeine chemische Verhalten eines Elementes aus seiner Stellung im Periodischen System, sowie aus Elektronenkonfiguration und Ionenpotential des einzelnen Ions hergeleitet wird, soweit das irgend angängig ist.

Wie aus dem Gesagten hervorgehen dürfte, spielt die theoretische Betrachtung der chemischen Vorgänge eine wesentliche Rolle und nimmt dementsprechend einen relativ breiten Raum ein. Allein der Allgemeinbehandlung der Grundlagen (Periodensystem,Massenwirkungsgesetz,elektrolytische Dissoziation, Löslichkeitsprodukt, Wasserstoffionenkonzentration, Hydrolyse, Puffergemische, Fällungen, Adsorption, Kolloide Lösungen, Mitfällung, Redoxreaktionen, Komplexverbindungen) sind 127 von insgesamt 518 Textseiten gewidmet. Aber auch in den weiteren Kapiteln, in denen die verschiedenen analytischen Gruppen behandelt werden, sind immer wieder theoretische Betrachtungen eingestreut. In dem Abschnitt „Analyse der Kationen" (270 Seiten) sind die Nachweisreaktionen für die Ionen von 31 Elementen angegeben und durchweg unter Angabe der Reaktionsgleichungen erläutert. Eine kurze Skizzierung der wesentlichen chemischen Eigenschaften der Elemente sowei eine allgemeine Charakteristik der einzelnen analytischen Gruppen ist jeweils vorangestellt. Die vielfach als zwei besondere Gruppen betrachteten Elemente der Ammoniak- und Ammoniumsulfidgruppe werden als eine gemeinsame Gruppe behandelt. In den systematischen Trennungsgängen für die Kationen der einzelnen Gruppen ist allerdings nicht auf alle Elemente, deren Nachweisreaktionen angegeben sind, Rücksicht genommen worden. Insofern entsprechen die hier gegebenen Trennungsschemata etwa dem Umfang der einfachen Schulanalyse. Die „Analyse der Anionen" (64 Seiten) behandelt in entsprechender Form die Verhaltensweise und die charakteristischen Reaktionen von 24 Anionen bzw. nichtmetallischen Elementen. In weiteren Kapiteln werden Angaben zur mikrochemischen Kristallanalyse (9 Seiten), zur Tüpfelanalyse (8 Seiten), zur Chromatographie (1 1/2 Seiten) und zur praktischen Durchführung qualitativer Analysen (22 Seiten) gemacht, wobei auch kurz auf die Untersuchung von Metallen, Legierungen und Mineralen eingegangen wird.

In dem Werk ist eine beträchtliche Fülle an Stoff in sehr übersichtlicher und verständlicher Form dargeboten. Man findet ferner viele Zahlenangaben über die Löslichkeiten analytisch interessierender Verbindungen, über Stabilitätskonstanten von Komplexen, Dissoziationskonstanten von Säuren und Basen sowie Redoxpotentiale. Einige kleinere Ungereimtheiten, wie in einzelnen Fällen die Angabe unterschiedlicher Zahlen für ein und dieselbe Größe an verschiedenen Stellen des Buches, werden sich bei einer späteren Auflage sicher beheben lassen.

Ein verständnisvolles Durcharbeiten dieses Buches wird für den Studenten zweifellos von großem Nutzen sein.

H. BODE (Hannover)

ANNOUNCEMENTS

THIRD CONFERENCE ON ANALYTICAL CHEMISTRY IN NUCLEAR REACTOR TECHNOLOGY

THE ANALYSIS OF REACTOR MATERIALS FOLLOWING THE OPERATION OF NUCLEAR REACTORS

The Oak Ridge National Laboratory has announced that the Third Conference on Analytical Chemistry in Nuclear Reactor Technology will be held at Gatlinburg, Tennessee, on October 26, 27 and 28, 1959.

The general theme of this conference, analysis of reactor materials following the operation of nuclear reactors, complements sequentially those of prior meetings which dealt with, (1) advances in the chemical analysis of important reactor materials, and (2) the role of analytical chemistry in the startup and operation of nuclear reactors.

The subjects which will be emphasized at this conference are: chemical analysis as related to the estimation of corrosion and erosion rates, reprocessing of fuels and blanket materials, and the analytical chemistry of fission product mixtures, of plubtonium, and of the transplutonic elements.

The contribution of papers pertaining to these or closely related subjects is solicited. Presentations on new developments or improvements in methods of chemical analysis, including advances in instrumentation, are especially invited although review papers and those involving pertinent theoretical discussions may well prove to be of equal interest and should be submitted for consideration.

To facilitate the completion and distribution of the program well in advance of the conference, speakers are requested to submit abstracts of about 500 words not later than August 1, 1959, and to indicate the time required for their presentation, not to exceed 30 min.

The Proceedings of the conference will be published. In order to be included in the Proceedings, manuscripts must be submitted prior to the opening of the conference. Publication in the Proceedings is not mandatory, but desirable. If a paper is not to be published in the Proceedings, the abstract and a reference to another source of publication, if any, will be made.

All communications relative to the conference, including the submission of manuscripts and abstracts, should be directed to: C. D. SUSANO, Oak Ridge National Laboratory, P. O. Box Y, *Oak Ridge*, Tennessee.

Inquiries with respect to accommodations or requests for reservations should be addressed to: Mr. TOM WOODS, Manager Mountain View Hotel, *Gatlinburg*, Tennessee.

Gatlinburg, Tennessee; October 26–28, 1959

TENTATIVE PROGRAM

At this stage in the development of the program, it is indicated that a morning and afternoon session will be held on each of the three days of the conference. If sufficiently greater interest is evidenced in certain aspects of this subject matter, arrangements will be made to increase the number of sessions but within the scheduled period of three days. Every effort will be made to avoid conflicts of interest in scheduling concurrent sessions.

Since it is intended that the scope of the program will necessarily encompass only a limited portion of the field of analytical chemistry as it pertains to the analysis of materials after they have been involved in an operating reactor, the general topics for each of the six sessions will be essentially as follows:

MONDAY, OCTOBER 26

Morning – The Analysis of Spent Reactor Fuels.
Afternoon – Analytical Chemistry of Exposed Blanket Materials.

TUESDAY, OCTOBER 27

Morning – Analytical Chemistry in the Reprocessing of Fuels and Blanket Materials.
Afternoon – The Analysis of Corrosion and Erosion Products.

WEDNESDAY, OCTOBER 28

Morning – The Analysis of Fission Product Mixtures.
Afternoon – Analytical Chemistry of Plutonium and Transplutonic Elements.

In addition to the formal technical program, an informal dinner and dance will be held on Tuesday evening. Arrangements are now being made to secure a prominent speaker, particularly in the field of analytical chemistry or some closely related field, to address the group after the dinner.

The conference is being conducted on an unclassified basis and all interested persons, regardless of affiliation, are invited to attend or participate in all or any portion of the meeting.

There will be no registration fee but, however, for those who partake of the dinner, a nominal charge will be made.

RUSSIAN JOURNAL OF INORGANIC CHEMISTRY

Starting with the January, 1959 issue, The Chemical Society is to publish, with the support of the Department of Scientific and Industrial Research, a cover-to-cover translation of the monthly journal, *Zhurnal neorganicheskoĭ Khimii*, a publication of the Academy of Sciences of the U.S.S.R. The translation will be undertaken for the Society by Infosearch Ltd., and the Society has appointed Professor P. L. ROBINSON as Executive Editor of the publication. Professor Robinson will be assisted by an advisory panel of distinguished inorganic chemists.

The sale and distribution of the journal will be undertaken by Cleaver-Hume Press Ltd., 31 Wright's Lane, London, W.8, from whom a detailed prospectus giving the scope of this journal may be obtained.

Translations will be issued in monthly parts as soon as possible after the Russian original is available. The subscription rate will be £ 30 (U.S.A. $ 90) per annum, but Universities and Technical Colleges may subscribe at a discount of 25%. Single issues can be purchased at £ 4 (U.S.A. $ 12) per copy to all purchasers.

The Society also hopes to start the publication within the next year of translations of the Russian "*Journal of Physical Chemistry*" (*Zhurnal fizicheskoĭ Khimii*) and "*Progress in Chemistry*" (*Uspekhi Khimii*).

VOL. 21 NO. 1 ANALYTICA CHIMICA ACTA JULY 1959

CONTENTS

Short Communications:

ELSEVIER PUBLISHING COMPANY, AMSTERDAM
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WILSON & WILSON

Comprehensive Analytical Chemistry

IN FIVE VOLUMES

Edited by

CECIL L. WILSON

Professor of Analytical Chemistry, The Queen's University, Belfast

and

DAVID W. WILSON

Sir John Cass College, London

This treatise on analytical chemistry is a comprehensive and self-sufficient work of reference, forming the natural starting point for any analytical investigation. All types of analytical methods, including classical, electrical, physical, optical and miscellaneous methods are thoroughly covered, both from the practical and the theoretical aspects, special attention being given to industrial applications. The wealth of literature references and excellent indexes further enhance the value of this monument in chemical literature.

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Part A: General Introduction. Analytical Processes. Gas Analysis.
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Part C: Gravimetric and Titrimetric Determination of the Elements.

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Volume 1 - Part C:	6 x 9"	approx. 700 pages	15 illustrations	November 1959		

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